









PROPERTIES OF STEAM  
AND  
THERMODYNAMIC THEORY  
OF TURBINES

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## PREFACE

My chief excuse for writing a book on the Properties of Steam is that the greater part of my life has been devoted to experimental and theoretical researches directly bearing on the subject, and to the training of rising engineers in physics and thermodynamics. The investigation of the properties of matter is the province of the physicist rather than of the engineer, and it is appropriate that the physicist should occasionally take a hand in discussing the application of the results to engineering problems. The discussion has been restricted to problems depending primarily on the properties of the working fluid, which are of fundamental importance, but are necessarily relegated to a secondary place in works dealing with the details of construction of machines. I hope for this reason that the present work may prove a useful supplement to treatises on Steam Power written from the engineering standpoint.

In the twenty years which have elapsed since the first publication of my equations for steam, the importance of the thermodynamical aspect of the problem has been more widely recognised. The extensive adoption of the turbine has raised a number of new problems, and many important researches have been published on the physical side. It was frequently suggested that my tables were becoming out of date and inaccurate in the light of subsequent knowledge, and already required serious alteration and revision. The original papers explaining the theory appeared in a variety of publications, some of which were difficult of access and were frequently misquoted. This gave rise to a number of misapprehensions which it was important to remove. I felt that I owed a duty to those who had done me the honour to adopt my system, to write a connected account of the theory and experiments on which it was based, to show how well it fitted with subsequent work, and how the equations and tables might best be applied to more recent developments. The defence of my work against common misapprehensions necessarily gives the book a personal character, which may be distasteful to some readers. In view of the circumstances, this was unavoidable, but it is less to be regretted because

## PREFACE

most of the objections raised afford good illustrations of thermodynamical principles and methods, which might otherwise appear devoid of practical interest.

I have been blamed in some quarters for delay in answering objections, which have sometimes been accepted as sound on account of my silence. This book was to have appeared in 1915 at the same time as the *Steam Tables*, but owing to the occupation of our buildings and equipment by Research Departments of the War Office, etc., my own time was entirely devoted to the work of national defence, and the absence of the junior staff of war service made it very difficult for me to obtain any assistance in the exacting work of reviewing the figures and calculations. The Table of Heat-Drop, VIII, in Appendix III, was calculated by my son G. S. Callendar, Sub.-Lieut., R.N.V.R. (now a first year student of the Imperial College). I have also to thank Miss M. Reeks, Technical Artist of the Imperial College, for valuable assistance in preparing some of the figures and diagrams. With these exceptions I am solely responsible for any mistakes or imperfections in the work, which I trust may be pardoned on account of the troublous conditions under which it was completed.

In the latter portion of the book, dealing with the Thermodynamical Theory of Turbines, some new methods have been introduced which I hope may prove useful to engineers. These are necessarily of a somewhat tentative character on account of the scarcity of suitable experimental data, but the results seem to correspond with practice so far as they can be tested, and it appears possible that they may have a wider application. An attempt has also been made to calculate the effects of superheat and super-saturation in a consistent manner. The latter have already been recognised by engineers, notably by Mr H. M. Martin in his *New Theory of the Steam Turbine*, but they appear to be more amenable to calculation than is usually supposed and to afford a promising field for experimental investigation.

H. L. CALLENDAR.

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## CHAPTER I

### INTRODUCTORY

#### NOTATION, UNITS AND CONSTANTS

**1. International Notation.** The symbolic notation adopted in this work is based as far as possible on the recommendations of the International Commission for the Unification of Physico-Chemical Symbols made at the meeting in Brussels in Sept. 1913. The list given in their report has been supplemented and extended along consistent lines by a special Committee of the Physical Society of London (*Proc. Phys. Soc.* 27, p. 205, 1915). The list is fairly complete as regards the science of heat, but the Committee recognise the necessity of using the same symbol with different meanings in different parts of a subject. A few such cases are indicated in the following list, with references to the chapters and sections in which the symbols occur.

#### ALPHABETIC INDEX OF SYMBOLS

- $A$  =  $1/J$ , reciprocal of mechanical equivalent of heat (II, § 8).
- $a$  = numerical factor for reducing  $PV$  to heat units (II, § 8).
- $B$  = constant of integration in expressions for  $E$  and  $H$  (III, §§ 19, 26).
- $b$  = covolume in characteristic equation (III, §§ 24, 28).
- $C$  = cooling-effect of Joule and Thomson (III, § 23).  
(Also consumption per horse-power-hour for a turbine (XV, § 161).)
- $c$  = coaggregation volume in characteristic equation (III, § 28).
- $D$  = finite drop or difference, e.g.  $DH$  = heat-drop (XIII, § 140).  
(Also diameter of a rotor or cylinder (XV, § 156).)
- $d$  = differential sign denoting an infinitesimal difference.
- $E$  = intrinsic energy of vapour per unit mass in heat units (II, § 8).
- $e$  = base of natural or hyperbolic logarithms.
- $F()$  = symbol for function, e.g.  $F'(t)$ , Carnot's function (VII, § 63).
- $F$  = relative efficiency, of a turbine (IX, § 94).
- $f$  = stage efficiency at any point of the expansion (XI, §§ 127-128).
- $G$  =  $T\phi - H$ , Gibbs' function or thermodynamic potential (VII, § 69).  
= acceleration of gravity (I, § 2).
- $H$  =  $E + aPV$ , total heat of vapour (II, §§ 8, 14).
- $h$  = total heat of liquid under saturation pressure  $p$  (II, § 11).
- $J$  = mechanical equivalent of heat (I, § 5).

*I* and *O* are not used as symbols owing to confusion with numerals 1 and 0.  
*K* and *k* (not being required in the present work for thermal conductivity and diffusivity, as recommended by the Committee) are employed for occasional constants and constant coefficients in the equations.

- L* = latent heat of vaporisation in thermal units (I, § 7; II, §§ 16-18).  
*l* = leakage clearance in a turbine (XV, § 157).  
*M* = mass-flow (lbs./sec. or kg./sec.) (X, § 99).  
*m* = index in equation  $PV = kP^m$ , or  $H - B = kP^m$  (IX, § 95).  
*N* = number of stages or pairs in an expansion (XI, § 126).  
*n* = index in  $c = (T_0/T)^n$ .  $S_0/R = n + 1 = 13/3$  for steam (I, § 7; III, § 28).  
*P* = pressure of vapour generally under any conditions.  
*p* = vapour-pressure of liquid, or saturation-pressure of vapour.  
*Q* = quantity of heat supplied per unit mass in thermal units (II, § 9).  
*q* = quality, or dryness-fraction of wet steam (VII, § 66).  
*R* = gas-constant, or limiting value of  $aPV/T$  at low pressures (I, § 7).  
 (Also used for rev./min. of a turbine (XV, § 156).)  
*r* = ratio of expansion or pressure (XII, § 135; XIII, § 143).  
 (Also used for radius of a wheel or tube (XI, § 129), etc.)  
*S* = specific heat of vapour at constant pressure (III, § 19).  
*s* = minimum specific heat of liquid (II, § 12).  
*T* = temperature reckoned from absolute zero (I, § 7).  
*t* = temperature reckoned from 0° Centigrade or Fahrenheit.  
*U* = velocity of fluid, ft./sec. or metres/sec. (II, § 10; X, § 98).  
*u* = velocity of blades in a turbine (XI, § 114).  
*W* = work done by vapour (II, § 10; VII, § 63; IX, § 84, etc.).  
*w* = work done on liquid in feed-pump (IX, § 93).  
*X* = cross-section of nozzle or annular area in a turbine (X, § 99).  
*x* = linear dimension of nozzle or annular area (XI, § 126, etc.).  
*Y* = surface tension of liquid (X, § 102).  
*y* = capillary elevation (VIII, § 80).  
*Z* = dimensional constants (XIV, § 145).  
*z* = velocity ratio (XI, § 114, etc.).  
*α* = discharge angle with axis.  
*β* = discharge angle with blade-ring (XI, § 115).  
*γ* = index in adiabatic equation  $PV^\gamma = K$  (X, § 99).  
*π* = ratio of circumference to diameter.  
*Σ* = symbol of summation of finite quantities (XV, § 156).  
*Φ* = entropy of vapour.  
*φ* = entropy of liquid (VII, § 66).

It is a matter of practical convenience to represent corresponding quantities for the vapour and liquid as far as possible by capitals and lower-case symbols respectively, because these commonly occur together in the same equations, and would otherwise have to be distinguished by using different letters, or by suffixes, which are frequently required for other purposes. It is not, un-

common in many books to see two or even three suffixes attached to the same symbol, which is extremely confusing to the reader, in addition to being troublesome to write or print.

Initial and final states in expansion may conveniently be distinguished by single and double dashes, provided that these do not interfere with numerical indices representing powers. Thus  $V'$ ,  $v'$ , represent initial volumes of vapour and liquid at  $P'$ ,  $T'$ , and  $V''$ ,  $v''$ , the final volumes at  $P''$ ,  $T''$ . Initial or limiting values, defined by the vanishing of some other quantity, are denoted by the suffix  $(_0)$ , thus  $S_0$  is the limiting value of  $S$  at  $P = 0$ , and  $H_0$  is the initial value of the total heat at zero velocity ( $U = 0$ ) in flow through a nozzle. The suffix  $(_s)$  is employed for indicating the state of dry saturated steam, thus  $V_s$ ,  $H_s$ ,  $\Phi_s$ , are the volume, total heat, and entropy of dry saturated steam. The suffix  $(_w)$  is similarly employed to imply that the steam is wet, but these suffixes may be omitted if the state is otherwise obvious, especially in the case of the liquid, for which  $h$  and  $v$  are always required under saturation pressure  $p$ .

**Abbreviations and References.** The three systems of units most commonly employed by engineers, are indicated by the abbreviations, K.M.C., F.P.C., and F.P.F., as explained in the next section.

References to scientific papers in periodicals are generally given in the form adopted by *Science Abstracts*, the editors of which have had great experience in this respect.

The author's original papers explaining the theory, which appeared (1) in the *Proceedings of the Royal Society*, Vol. 67, pp. 266-286, June, 1900, and (2) in the articles, Calorimetry, Thermometry, Thermodynamics, and Vaporisation in the *Encyclopaedia Britannica*, 10th edition, 1902, requiring frequent citation, are referred to in the present work by the abbreviations (*R. S.* 1900), and (*E. B.* 1902), respectively.

A list of other scientific papers by the author, directly bearing on the subject of this work, is given at the end of the book. The reader must refer to these papers for experimental details which, though essential to accuracy, are not of sufficient general interest for reproduction.

*Cross references* in the body of the work are generally made to the sections, which are numbered continuously throughout the book. The equations and tables in each chapter are numbered in separate series, and are referred to when necessary by the number



of the chapter in roman type with the number of the equation in brackets.

In order to avoid repetition, the majority of the purely mathematical relations required in the course of the work, are collected in Appendix I, Thermodynamical Relations, where they are developed as a connected series. It is hoped that this procedure will render the relations themselves more intelligible to the student, and will serve as an introduction to the practical use of partial differential coefficients in thermodynamics.

Directions with regard to the use of the Steam Diagram, issued with this book, are collected in Appendix II; and the Steam Tables, with a summary of the more important equations, are collected in Appendix III to facilitate reference. The greater part of these two appendices has already been published separately (Edward Arnold, 1915).

**2. Systems of Units.** One of the chief difficulties in reducing the results of different experimentalists, or comparing values given in different Steam Tables, arises from the fact that they are often expressed in different systems of units, and that the fundamental quantities involved are not always defined in precisely the same way. It is therefore necessary to explain with some care the system of units adopted as the basis of the present work, the selection of the fundamental constants from experimental data, and the theory by which the values given in the tables have been calculated.

The Centimetre-Gramme-Second, or C.G.S. system of units, is now almost exclusively adopted for scientific purposes, and is generally used, in conjunction with the Centigrade scale of temperature, for expressing the results of the most accurate experiments. But the systems most in vogue among steam-engineers are (1) the Foot-Pound-Fahrenheit (F.P.F.) system, (2) the Foot-Pound-Centigrade (F.P.C.) system, and (3) the Kilogramme-Metre-Centigrade (K.M.C.) system. The K.M.C., or Metric system, is naturally employed by Continental nations who have adopted the metric system of weights and measures for all their machines and measuring instruments. The F.P.F., or British system, was at one time exclusively adopted by engineers in English-speaking countries, where nearly all the machines and measuring instruments are still constructed and graduated according to the British system of weights and measures, and where the Fahrenheit scale is the most familiar scale of temperature. The F.P.C. system is now largely

employed in English text-books, and is gradually displacing the F.P.F. system among engineers, owing to the superior simplicity of the Centigrade scale, and the great convenience of expressing all quantities of heat-energy by the same numbers as those employed by Continental engineers and in accurate scientific work. It is a comparatively simple matter to change the thermometric scale, but it is out of the question at present to discard the foot and the pound, which are in other ways very convenient units for steam. The Foot-Pound-Centigrade system has accordingly been adopted for general purposes in the present work as the most suitable compromise, because it greatly facilitates reduction to either of the other systems when exact comparisons are required. But in the majority of important cases the corresponding values and formulae in the other two systems have also been given.

*Reduction Factors.* In constructing the Steam Tables, the following factors have been employed as being sufficiently accurate for the purpose in reducing and comparing experimental results expressed in different systems.

Length, 1 foot = 0.304800 metre,

Mass, 1 pound = 0.453592 kilogramme,

from which we obtain the factor for Density or Specific Volume,

Density, 1 pound per cu. ft. = 16.0184 kilos per cu. metre,

Specific Volume, 1 cu. metre per kilo. = 16.0184 cu. ft. per lb.

The unit of Pressure, expressed in terms of weight per unit area, (pounds per sq. in., or kilograms per sq. cm.) depends on the value of the intensity of gravity assumed at the place of observation. English engineers generally take the intensity of gravity at mean sea level in London as the standard. The value of gravity varies appreciably along any given parallel of latitude, so that it is necessary to specify a particular place or value assumed. American and Continental engineers generally take the conventional value of the acceleration of gravity at sea level in latitude 45°, namely 980.665 C.G.S. The acceleration of gravity at sea level in London exceeds this conventional value by 1 part in 2000, or may be taken as 981.16 C.G.S. with an accuracy sufficient for the present purpose. This is equivalent to 32.190 ft./sec.<sup>2</sup>. One pound per sq. in. at London, and one foot-pound at London have been taken in the tables as the units of pressure and work. The values of pressure given in the tables must accordingly be increased by one part in

2000 if it is required to reduce them to the corresponding conventional values in latitude  $45^{\circ}$ .

The reading of a pressure-gauge generally represents the difference from atmospheric pressure at the time of observation. The pressure in excess of atmospheric is commonly called the gauge pressure, the defect below atmospheric pressure is commonly called the vacuum.

The absolute pressure reckoned from zero is the quantity required in most calculations and experiments. To find the absolute pressure it is usually necessary to read the barometer, and deduce the atmospheric pressure by applying suitable corrections for temperature and gravity. The absolute pressure is deduced by adding the atmospheric pressure (expressed in the same units) to the gauge-pressure, or by subtracting the vacuum from the atmospheric pressure.

Readings of gauge-pressure or vacuum are often stated with reference to a barometric standard of 30 inches of mercury, which at  $62^{\circ}$  F. is equivalent to 14.690 lbs./sq. in., or is practically equal to one standard atmosphere in the latitude of London. But 30 inches of mercury at  $0^{\circ}$  C. or  $32^{\circ}$  F. is equivalent to 14.730 lbs./sq. in., which is appreciably different.

Barometers for meteorological purposes are often graduated in millibars, 1000 millibars being equal to the C.G.S. atmosphere of one megadyne per sq. cm., which is very nearly equivalent to 760 mm. of mercury at  $0^{\circ}$  C. in latitude  $45^{\circ}$ , or to 14.496 lbs./sq. in. in London.

The reading of the barometer, and the correction of mercury columns for temperature, are frequently of considerable importance at low pressures. Thus at 28 inches vacuum an error of a tenth of an inch in both barometer and vacuum-gauge may make an error of 10 per cent. in the corresponding value of the absolute pressure.

High pressures are frequently stated in atmospheres, and low pressures sometimes in percentage of an atmosphere. It is desirable in such cases to specify the kind of atmosphere intended. The term atmosphere should not be used as synonymous with a pressure of 1 kg./sq. cm., which differs by 3.8 per cent. from the standard atmosphere of 760 mm.

The temperature of  $100^{\circ}$  Centigrade is defined as being that at which the pressure of saturated steam is one Standard Atmosphere or is equivalent to a column of mercury 760 mm. high, of standar

density 13.59545 grams per cu. cm. (corresponding to  $0^{\circ}\text{C}.$ ), at a place where the acceleration of gravity is 980.665 C.G.S. This pressure is equivalent to 14.6890 pounds weight per sq. in. at London, or to 14.6964 in latitude  $45^{\circ}$ .

We have therefore the following reduction factors for pressure and work,

1 atmosphere (760 mm. Hg, lat. $45^{\circ}$ )	=	14.6890 lbs./sq. in. (London),
1 lb./sq. in. (London)	=	.070307 kg./sq. cm. (London),
" "	=	.070312 kg./sq. cm. (lat. $45^{\circ}$ ),
1 foot-pound (London)	=	.138255 kilogrammetre (London),
" "	=	.138324 " (lat. $45^{\circ}$ ).

**3. Units of Heat.** It is taken as axiomatic that the quantity of heat required to raise the temperature of a given mass of a particular substance through a given range must always be the same under the same conditions, and may therefore be made the basis on which quantities of heat are measured.

The unit of heat generally adopted in scientific work is the quantity of heat required to raise the temperature of 1 gramme of water under a constant pressure of 1 atmosphere by  $1^{\circ}\text{C}.$ , measured on the scale of the standard hydrogen thermometer in the neighbourhood of some particular temperature, generally either  $15^{\circ}$ , or  $20^{\circ}\text{C}.$  These two units differ slightly in value and are generally referred to as the "gram-calorie at  $15^{\circ}\text{C}.$ " and the "gram-calorie at  $20^{\circ}\text{C}.$ " respectively when great precision is required. Instead of the gram, the kilogram, or the pound, may be taken as unit of mass, in which case the unit is called the "kilocalorie" or the "pound-calorie."

The British thermal unit, or B.Th.U., is defined in practically the same way in terms of the pound and degree Fahrenheit. It is seldom used for scientific purposes, but may be taken as  $\frac{5}{9}$  of the pound-calorie under similar conditions.

The calorie at  $20^{\circ}\text{C}.$  is the most suitable unit for accurate calorimetric work at ordinary temperatures. But for expressing the properties of steam, the MEAN CALORIE, which is generally defined as one-hundredth part of the quantity of heat required to raise the temperature of unit mass of water from  $0^{\circ}$  to  $100^{\circ}\text{C}.$ , is the most convenient unit. The mean calorie has the advantage that its definition depends only on that of the fixed points, and that it simplifies the expression for the "heat of the liquid." This unit has accordingly been adopted as the basis of the present work.

**4. Variation of Specific Heat of Water.** The relation between these units of heat is of primary importance in accurate calorimetry, and is required in the construction of steam tables for determining the values of the fundamental constants to be employed. Since the accurate comparison of the units of mass presents no difficulty, the problem is reduced to that of determining the variation of the specific heat of water with temperature measured on the gas-scale. It might be thought at first sight an easy matter to determine the required variation by simply mixing known quantities of water at different temperatures in a calorimeter. But when this is done at temperatures above  $50^{\circ}\text{C}$ . the thermometric difficulties are considerable, and the calorimetric errors due to evaporation or to heat-loss in transference of the hot water to the calorimeter, become so uncertain that this method has led, even in the hands of skilful experimentalists, to most discordant results. The experiments of Regnault were most carefully performed, and were for many years accepted as the standard, but he was unable, owing to the defective state of thermometry, to detect with certainty any variation of the specific heat of water between  $0^{\circ}$  and  $100^{\circ}\text{C}$ ., or any systematic divergence of the scale of the mercury thermometer from the gas-scale between these limits. From his experiments on the total heat of water between  $100^{\circ}$  and  $200^{\circ}\text{C}$ ., he was led to infer a gradual rise of specific heat from  $0^{\circ}$  to  $100^{\circ}\text{C}$ ., but his experiments failed to give any direct or reliable information with regard to the variation of specific heat between  $0^{\circ}$  and  $40^{\circ}\text{C}$ . In calorimetric work a great deal depends on the accurate observation of small differences of temperature, for which the mercury thermometer is not well suited, owing to its errors of stem-exposure, and to its temporary variations of zero, which had not been sufficiently studied in Regnault's time. Even when special attention has been paid to these thermometric difficulties, as in Lüdin's experiments (Inaugural Dissertation, Zürich, 1895), the method of mixtures has not given satisfactory results. Thus Lüdin's observations show a rapid fall of specific heat near the boiling-point, which is probably erroneous. The most consistent results have been obtained by observing the rise of temperature due to the supply of measured quantities of electrical or mechanical energy. These methods are intimately associated with the determination of the mechanical equivalent of heat, a problem of primary importance in the theory of the steam-engine, which requires more detailed consideration.

**5. The Mechanical Equivalent of Heat.** Joule showed by a considerable variety of experiments between the years 1842-1850 that, whenever heat was generated by friction, the quantity of heat produced was, within the limits of experimental error, proportional to the quantity of mechanical work expended, and was independent of the nature of the materials employed and of other conditions. He also showed that the same coefficient of proportionality between work and heat applied when the conversion was effected by means other than friction. His final result, obtained by friction of water (*Phil. Trans.*, 1850), was that 772.5 foot-pounds of work at Manchester were equivalent to the quantity of heat required to raise one pound of water  $1^{\circ}$  F. in temperature at  $62^{\circ}$  F. on the scale of his mercury thermometers. At a later date, when the absolute value of the British Association Unit of electrical resistance had been determined, experiments by the method of electric heating were found to give a smaller result than Joule's for the mechanical equivalent. At the request of the British Association Joule accordingly repeated his experiments in 1878 on a larger scale, but found the same result as before. The error was subsequently found to lie chiefly in the determination of the B.A. unit of electrical resistance. Joule's result, when reduced to the scale of the gas-thermometer and latitude  $45^{\circ}$ , must be raised to about 776 foot-pounds per pound-Fahrenheit unit, but this correction is somewhat uncertain as the scale of his mercury thermometers could not be tested under the exact conditions of the original experiments.

Rowland, in repeating Joule's experiment in 1879 on a larger scale, with many refinements, over an extended range of temperature from  $5^{\circ}$  to  $35^{\circ}$  C., discovered the previously unsuspected fact, of vital importance in accurate calorimetry, that the specific heat of water diminished from  $5^{\circ}$  to  $30^{\circ}$  C. by nearly 1 per cent., instead of increasing continuously from the freezing point as had previously been assumed. His experiments were probably most accurate in the neighbourhood of  $20^{\circ}$  C., where the uncertainty of reduction is of the order of 1 in 2000 only. He made the kilocalorie at this temperature on the gas-scale equivalent to 426.2 kilogrammetres in latitude  $45^{\circ}$ , or the pound-Fahrenheit unit equivalent to 776.8 foot-pounds under the same conditions, a result agreeing remarkably well with that of Joule.

Expressed in absolute units on the C.G.S. system, which are the most convenient and the most commonly adopted for comparison,

Rowland's value of the equivalent of the gram-calorie at 20° C is 4.180 joules, the joule being defined as 1 watt-second of electric energy, or  $10^7$  ergs C.G.S.

The equivalent of the *mean thermal unit* (0° to 100° C.) in mechanical energy was directly determined by Reynolds and Moorby (*Phil. Trans.*, 1898) by heating a measured stream of water from the freezing to the boiling point in a Froude-Reynolds hydraulic brake mounted on the shaft of a 100 H.P. steam-engine. In spite of the difficulties of accurate measurement on so large a scale with the calorimeter at the boiling-point, they succeeded in obtaining a result comparable in accuracy with that of Rowland at ordinary temperatures. When allowance is made for the fact that the water was not supplied exactly at the freezing point (where its specific heat varies somewhat rapidly with temperature) the value which they gave for the mean gram-calorie in absolute units may be taken as 4.184 joules, which is equivalent to 426.6 kilogrammetres per kilocalorie, or to 777.6 foot-pounds per B.Th.U. in latitude 45°. In order to compare this result with that of Rowland, it is necessary to know the variation of the specific heat from 0° to 100°, or at least the ratio of the specific heat at 20° C. to the mean over the whole range. Lüdin's formula (*loc. cit.*) gives 1.0063 for the ratio of the mean calorie to that at 20° C., which would make the mean-calorie equivalent to 4.206 joules, if the calorie at 20° C. is 4.180. The discrepancy between 4.206 and 4.184 is beyond the probable limits of error of Reynolds' and Moorby's experiments, and may be taken as an indication that Lüdin's formula is incorrect. Better agreement has been obtained by electrical methods of measurement.

**6. Electrical Methods of Calorimetry.** Griffiths (*Phil. Trans.*, 1895), and Schuster and Gannon (*Phil. Trans.*, 1896) measured the rise of temperature produced by passing an electric current through a resistance immersed in water in a calorimeter, and deduced values of the mechanical equivalent of the gram-calorie from those of the electrical standards employed. If their results are corrected for an error (at that time suspected, and subsequently proved) in the electromotive force of the Clark Standard cell, they become

Griffiths,                      gram-calorie at 20° C. = 4.187 joules,

Schuster and Gannon, gram-calorie at 19° C. = 4.188 joules.

Griffiths' observations extended over the range 15° to 25° C.

confirmed Rowland's results for the diminution of the specific heat of water over this range of temperature.

In the continuous electric method\* of Callendar and Barnes, a steady current of water passing through a fine tube is heated by an electric current through a central conductor. The difference of temperature between inflow and outflow is taken by a single reading of a pair of differential platinum thermometers, which permits a much higher order of accuracy than is obtainable with mercury thermometers. The annexed Fig. 1 shows a diagram of the arrangement. The flow-tube and thermometer pockets at either end are hermetically sealed in a vacuum-jacket to minimise external loss of heat. The method possesses special advantages for observing the variation of the specific heat, because the external water jacket surrounding the calorimeter can be maintained by a regulator at any temperature at which the specific heat is required. The absolute electromotive force of the standard cells employed was determined at the same time by King† with an electro-dynamometer specially designed by the author for the purpose, and was probably correct to 1 in 10,000. King's work has recently been verified by Prof. Norman Shaw‡, who has succeeded in obtaining a very high order of accuracy with the same instrument.

The results obtained by this method for the specific heat of water at various temperatures are indicated in Fig. 2. The values of the total heat deduced from the specific heat agreed with Rowland's values to one-hundredth of a calorie over the range 5° to 80° C. The result obtained for the equivalent of the mean gram-calorie over the range 0° to 100° C., was 4.1868 joules, exceeding that found by Reynolds and Moorby by less than 1 in 1000, which is probably within the limits of error of their experiments.

Dieterici (*Ann. Phys.*, 16, p. 593, 1905) employing an electrical method with an ice-calorimeter, reading to about 1 in 1000, subsequently found the result 4.1925 joules for the equivalent of the mean gram-calorie.

Adopting the value 4.1868 joules as the equivalent of the mean gram-calorie in absolute units, we obtain the following value for the pound-calorie:

1 mean Pound-Calorie (0° to 100° C.) = 1400.00 foot-pounds (London).

Callendar and Barnes, *B. A. Reports*, 1897, p. 552, and 1899, p. 624; *Phil. Trans.*, 1902, pp. 58-263; also Bakerian Lecture, *Phil. Trans.*, 1913, pp. 1-32.

\* *Phil. Trans.*, 1902, p. 81.

‡ *Phil. Trans. A*, 214, pp. 147-198.



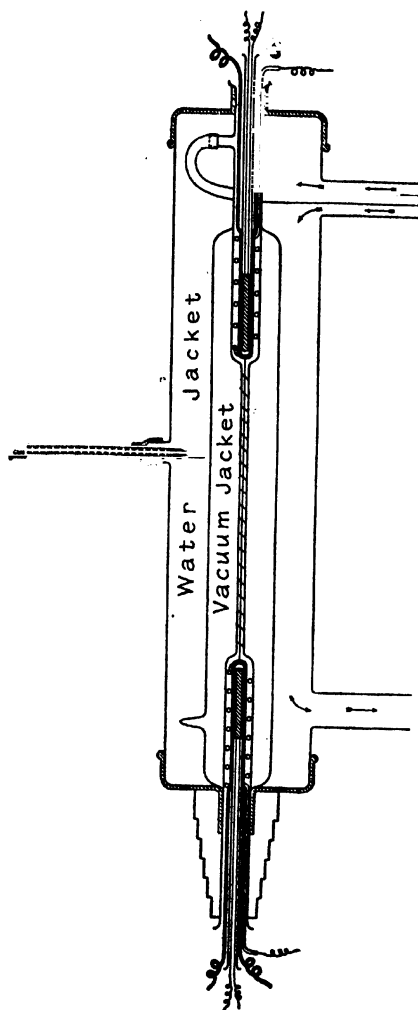


Fig. 1. Continuous Flow Electric Calorimeter.

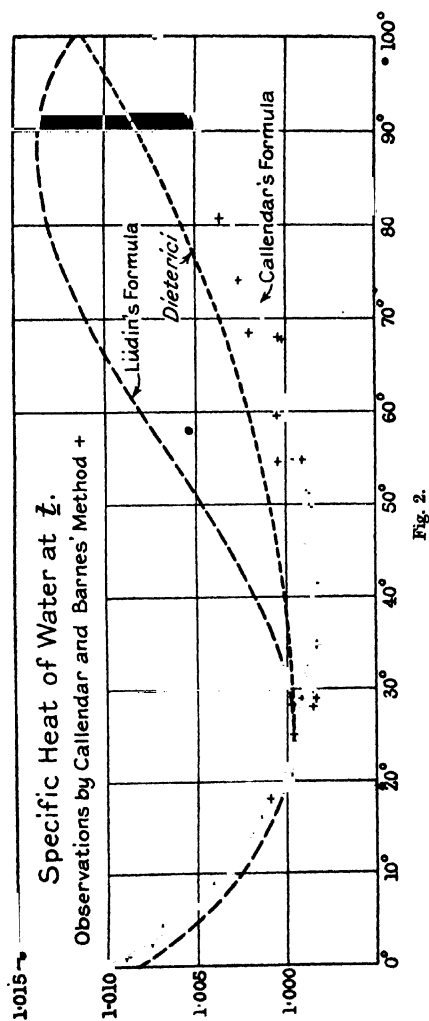


Fig. 2.

Owing partly to the great convenience of having an exact round number for the mechanical equivalent, this value has been adopted in the present work. The corresponding value in latitude  $45^\circ$  would be 1400.7 foot-pounds, and for other units

$$\begin{aligned} 1 \text{ mean B.Th.U.} &= 1400 \times \frac{1}{2} = 777.78 \text{ foot-pounds (London)} \\ &= 778.17 \text{ foot-pounds (lat. } 45^\circ), \end{aligned}$$

$$1 \text{ mean kilocalorie} = 426.98 \text{ kilogrammetres (lat. } 45^\circ).$$

**7. The Absolute Scale of Temperature.** A necessary preliminary to all accurate calculations for gases and vapours is the definition of the scale of temperature employed. This is generally defined in practice as that of the hydrogen thermometer below  $100^\circ \text{C.}$ , and as that of the nitrogen thermometer at higher temperatures. A discussion of all the available data in a paper\* read before the Physical Society of London in March 1901 led to the conclusion that intervals of temperatures reckoned on these thermometers from the freezing point upwards agreed with the absolute thermodynamic scale almost, if not quite, within the limits of error of experiment. It is generally assumed that thermometric readings are reduced to the scale of one of these gases, and it would be useless for the present purpose to attempt further reduction to the absolute scale. Since gas thermometers are quite unsuitable for the majority of experiments, the reduction to the hydrogen or nitrogen scale is generally effected in practice by comparison with a platinum thermometer, or preferably by the direct use of a platinum thermometer, if accuracy is required. If the reading of the platinum thermometer  $pt$  is reduced to true temperature  $t$  by means of the formula†,

$$t - pt = 1.50t(t - 100) \times 10^{-4},$$

the experience of many independent observers has shown that the values of  $t$  obtained agree with temperatures on the absolute scale within the probable limits of error of experiment.

The value of the freezing point of water in degrees Centigrade reckoned from the absolute zero of temperature, or the number to be added to the temperature  $t$  reckoned from  $0^\circ \text{C.}$  in order to obtain the temperature  $T$  on the absolute scale, was taken as

\* Published *Phil. Mag.*, Jan. 1903.

† *Phil. Trans. A*, 1887. This scale has recently been adopted by the Reichsanstalt, Berlin, April 1, 1916, as the official scale of temperature for accurate testing of thermometers.

273.0 in the author's original paper (*R. S.* 1890), in accordance with the value given by Lord Kelvin (*E. B.* 1882). It was shown, however, in the paper above referred to, that the true value was certainly within two or three-hundredths of a degree of 273.10. The difference is quite appreciable in accurate reductions, and the value 273.10 has accordingly been employed for the present work. This value has been verified, within the above limits, by many subsequent computers, though the exact values given are to some extent a matter of taste, depending on the weights attached to the various series of observations on which the results are based. We, therefore, employ the formulæ

$$T = t + 273.10^{\circ} \text{C.} = t + 459.58^{\circ} \text{F.}$$

Most of the fundamental constants required in calculating the properties of steam depend directly or indirectly on the values selected for the mechanical equivalent and for the absolute zero of temperature, as well as on the unit of heat. The determination of each constant is liable to errors of experiment, which will be discussed in the following chapters. For these reasons the absolute values, even of the best determined constants, such as  $R$  and  $L$  at  $100^{\circ} \text{C.}$ , are uncertain by at least 1 part in 2000. But in order to obtain relative values in the tabulation of the various properties, sufficiently exact and consistent for the investigation of problems depending on small differences, it is necessary to take the values of the fundamental constants to five significant figures, and to work the results in each case to a hundredth of a thermal unit.

The values adopted for the most important of these constants are:

Latent heat at B.P.,  $L = 539.80 \text{ C.}, = 970.74 \text{ F.},$

Gas constant for steam per unit mass,  $R = 0.11012,$

Specific heat at zero pressure,  $S_0 = 0.47719,$

Ratio  $S_0/R = n + 1 = 13/3,$  Index  $n = 10/3.$

The value of  $L$  depends on the scale of temperature, whether Centigrade or Fahrenheit, but those of  $R$  and  $S_0$  are independent of the temperature scale, and are the same in all practical systems of units, when expressed in terms of thermal units per degree. The value of  $R$  for steam can be estimated from the molecular weight in terms of hydrogen and oxygen. The limiting value of  $aPV/T = R$  at low pressures is found for  $\text{O}_2$  or  $\text{N}_2$  by calculating the value at N.T.P. from the observed density, and correcting the value of  $PV$  to zero pressure by Amagat's coefficient. The value of  $R$  for steam

is found by multiplying the result for  $O_2$  by the ratio  $O_2/H_2O$  of the molecular weights. Values obtained in this way from different data agree to about 1 in 2000. The value of  $S_0$  is variable to a slight extent with temperature, but the range of variation according to different experiments is uncertain, and is of little practical importance for the present purpose. A mean value is accordingly selected, having a simple ratio to  $R$ , in order to simplify the adiabatic equation, as explained in Chapter III, § 25.

## CHAPTER II

### THE TOTAL HEAT OF WATER AND STEAM

**8. Intrinsic Energy and Total Heat.** In accurate calorimetric work, especially with gases and vapours, it is often important to define the exact nature of the quantity measured, which depends on the conditions of pressure and volume as well as on the temperature.

The quantity of energy existing in a body in a given state is called the internal or intrinsic energy, and is denoted by the symbol  $E$  when measured per unit mass. The intrinsic energy  $E$  per unit mass is commonly expressed in thermal units, e.g. in pound-calories Centigrade per pound, but the Centigrade unit of intrinsic energy may be more briefly referred to as the calorie-Centigrade, because it is obviously independent of the unit of mass. The number representing the intrinsic energy of any substance in a particular state is evidently the same whether expressed in pound-calories per pound or in kilogram-calories per kilogram, provided that the same scale of temperature is employed in both cases. When however it is required to reduce the intrinsic energy expressed in Centigrade calories to British thermal units, the value in Centigrade calories must be multiplied by the factor 1.8 or  $\frac{9}{5}$  to reduce to the Fahrenheit scale.

The state of a substance may in general be sufficiently defined by the pressure  $P$  and the volume  $V$  of unit mass. The product  $PV$  has a definite value for any particular state of the substance considered, and represents the work done in forcing unit mass into an enclosure against a steady pressure  $P$ . The product  $PV$  is obtained in foot-pounds if the pressure is expressed in pounds weight *per sq. ft.* and the volume  $V$  in cubic feet. More commonly the pressure is expressed in pounds *per sq. in.*, in which case the work done is  $144PV$  foot-pounds. This may be reduced to its equivalent in mean pound-calories by dividing by 1400, the equivalent of the mean calorie in foot-pounds. The letter  $A$  is very commonly employed to represent the reciprocal of the mechanical equivalent (in this case  $1/1400$ ), which has different numerical values in

different systems of units. The letter  $a$  will be employed to denote the numerical factor (144/1400 on the F.P.C. system, or its equivalent, in other systems) required to reduce the product  $PV$  to calories when  $P$  and  $V$  are expressed in arbitrary units. These numerical factors are very often omitted altogether in books on thermodynamics, because it is tacitly assumed that all the terms in any physical equation must be expressed in the same units; but in a work like the present it will be more convenient to indicate them by special symbols ( $a$ , etc.) explicitly in the equations.

The reduction factor  $a$  is that most often required in thermodynamical equations. Nearly all the equations in this book will give consistent results in any practical system of units, not only for  $P$  or  $V$ , but also for any of the other quantities concerned, provided that the appropriate numerical value of the reduction factor  $a$  is employed for each system.

When the unit of  $H$  or  $E$  is the mean caloric Centigrade, the values of the reduction factor  $a$  are as follows for various units of  $P$  and  $V$ , as previously defined:—

Unit of $P$	Unit of $V$	Unit of $PV$	Value of $a$	Reciprocal of $a$	System of units
1 lb./sq. in.	1 cu. ft./lb.	144 ft. lbs./lb.	144/1400	0.7222	F.P.C.
1 kg./sq. cm.	1 cu. m./kg.	10000 kgm./kg.	10000/426.7	0.04267	K.M.C.
760 mm. Hg	1 litre/gm.	101.33 J./gm.	24.20	0.04132	Atmo-litre
1 mm. Hg	1 cu. cm./gm.	1333.3 erg/gm.	$3.185 \times 10^{-8}$	31400	
1 in. Hg	1 cu. ft./lb.	70.7 ft. lbs./lb.	0.0505	19.80	

When the unit of  $H$  is the mean B.Th.U., the value of  $a$  on the F.P.F. system (with  $P$  in lbs./sq. in.) is  $144/777.8 = 1/5.4012$ . If the unit of  $P$  is the weight of unit mass on one face of the unit cube (e.g. 1 lb./sq. ft. with  $V$  in cu. ft./lb.) the value of  $a$  is the reciprocal of  $J$ ; but this unit of pressure, though often employed in equations, is inconvenient in practice, and is seldom used in graduating pressure-gauges.

In writing an equation, it is usually most convenient to insert the factor  $a$  explicitly, as in  $aPV$ , but in working a term of this form, or of the form  $R/aV$ , on a slide-rule, it is generally more convenient to employ the reciprocal of  $a$ , as given in the above table, because the operation  $P \div (1/a) \times V$ , or  $R \div V \times (1/a)$ , requires fewer settings of the slide than the direct multiplication  $a \times P \times V$ , or the division  $R \div a \div V$ .

The value of  $a$  in any other system of units is the ratio of the work equivalent of the product of the units of  $P$  and  $V$  to the

mechanical equivalent of the thermal unit expressed in the same work units as  $PV$ .

The necessity of repeating an equation in different systems of units is in most cases avoided by inserting the symbol  $a$  for the reduction factor. This method will be found to save a great deal of uncertainty and loss of time in the numerical application, and in the comparison of results of different experiments, expressed in various systems of units.

The intrinsic energy  $E$  may also be expressed in foot-pounds or other units of work by multiplying the value in thermal units by the appropriate value of the mechanical equivalent  $J$ , or dividing by  $A$ . It may also be directly measured in mechanical units by electrical or mechanical methods. But it is most commonly expressed and measured in thermal units, and it may be assumed that it is expressed in Centigrade calories throughout this work unless it is otherwise specifically stated.

The total heat denoted by  $H$  is defined as the sum,  $E + aPV$ , of the intrinsic energy  $E$  and the work  $aPV$  expressed in the same units. The total heat is the quantity generally tabulated for steam, because it is more often required in steam-engine practice, and also more easily measured in calorimetric experiments, than the intrinsic energy. It will always be expressed, like the intrinsic energy, in Centigrade calories, unless otherwise stated, and may be reduced to other units by the same factors as in the case of intrinsic energy. The total heat thus defined is a function of great generality and importance in thermodynamics, but it does not exactly correspond with Regnault's definition of the total heat of steam, which refers only to a special case. Some writers use the term "total energy" for the quantity  $E + aPV$ , for the sake of distinction, retaining the term "total heat" in the special sense of Regnault's definition. But the term "total energy" appears to be more appropriate for the sum of the total heat  $E + aPV$ , and the kinetic energy  $AU^2/2g$  (expressed in calories), when the fluid is moving with velocity  $U$ . The kinetic energy is a very important factor in many steam problems, and it is useful to include it in the term "total energy." The advantages gained by adopting the wider definition of total heat\* (including Regnault's total heat of steam as a special case) are so great that the term total heat and the symbol  $H$  are now generally used as denoting the function  $E + aPV$ .

\* *Phil. Mag.*, 1903, p. 50. *E. B.*, 1902, *Thermodynamics and Vaporization*, vol. 33, pp. 285 and 628.



9. **Calorimetric Measurement of  $E$  and  $H$ .** When a quantity of heat  $MQ$  is supplied to a body of mass  $M$ , the whole of the heat goes to increase the intrinsic energy, say from  $E_1$  to  $E_2$ , provided that there is no external work done by expansion or otherwise. The quantity of heat  $Q$  supplied under this condition per unit mass, divided by the rise of temperature, is called the mean specific heat at constant volume over the range of temperature considered, and is equal to the increase of intrinsic energy per degree at constant volume.

If on the other hand the body is allowed to expand, say from specific volume  $V_1$  to specific volume  $V_2$ , under a constant external pressure  $P$ , part of the heat  $Q$  supplied per unit mass is expended in performing external work, which is equivalent to  $aP(V_2 - V_1)$  per unit mass when reduced to calories. We have therefore the equation

$$\begin{aligned} Q &= E_2 - E_1 + aP(V_2 - V_1) \\ &= (E_2 + aPV_2) - (E_1 + aPV_1) = H_2 - H_1, \dots\dots\dots(1) \end{aligned}$$

which is simply the expression of the law of conservation of energy.

The expression on the right hand side is the change of total heat at a constant pressure  $P$ . The heat supplied per unit mass at constant pressure divided by the rise of temperature is called the mean specific heat at constant pressure, and is equal to the increase of total heat per degree at the same constant pressure. It is seldom practicable to keep the volume of a liquid or solid constant while it is being heated, so that the change of intrinsic energy at constant volume cannot as a rule be measured directly by experiment. But it is nearly always possible to keep the pressure constant, and to observe the specific heat at constant pressure, or the increase of the total heat, from which the change of intrinsic energy may be deduced if required. In the case of solids and liquids, the changes of volume are small, and the difference between the total heat and the intrinsic energy is comparatively unimportant at moderate pressures. But in the case of gases or vapours the difference may be of great importance, on account of the large changes of volume. For instance, in the case of water, the expansion from  $0^\circ$  to  $100^\circ$  C. under atmospheric pressure is 4.8 per cent. of the volume at  $0^\circ$  C. The term  $aP(V_2 - V_1)$ , (taking  $a = 144/1400$ ,  $P = 14.70$  lbs./sq. in.,  $V_1 = .01602$  cu. ft./lb.,  $V_2 - V_1 = .048V_1$ ), reduces to .00105 of a calorie, which is only 1 part in 100,000 of the increase of total heat, namely 100 calories. The change of intrinsic energy at constant

pressure is for all practical purposes the same as that of total heat in this particular case, but in the case of a gas or vapour the two may differ by 30 per cent. or more, and it must not be hastily inferred that the distinction is immaterial even in the case of a liquid or solid.

Thus, if the volume of water could be kept constant while it was heated from  $0^{\circ}$  to  $100^{\circ}$  C., the pressure would increase by about 850 atmospheres, and the increase of  $H$  would be greater than that of  $E$  by the term  $a(P - P_0)v_0$ , which amounts to about 21 cal. The actual increase of  $H$  would be about 15 calories greater than in the previous case in which the water was heated under a constant pressure of one atmosphere, and that of  $E$  would be about 6 calories less.

In work of precision it is usual to define the pressure under which the measurements are made, though the effect of pressure, in the case of a liquid like water at ordinary temperatures, is too small to be detected in the majority of experiments. The usual definition of the mean calorie is equivalent to one-hundredth part of the change of total heat of water when heated from  $0^{\circ}$  to  $100^{\circ}$  C. under a constant pressure of one standard atmosphere. But since the accuracy of a calorimetric experiment rarely surpasses 1 in 1000, the calorie might equally well be defined for most practical purposes in terms of the change of intrinsic energy under the same conditions.

In the present work, the unit of heat in terms of which the total heat of water is expressed has been taken as one-hundredth part of the change of total heat of water between  $0^{\circ}$  and  $100^{\circ}$  C. when the water is heated under the pressure of its own vapour only. The quantity of heat required in this case exceeds that required when the pressure is kept constant and equal to one atmosphere, by the small quantity  $a(p_{100} - p_0)v_0$ , which amounts to 0.024 cal. or about one part in 4000 of the whole. The mechanical equivalent of the mean gram-calorie thus defined is taken as 4.1868 joules, in which case that of the mean gram-calorie under atmospheric pressure would be 4.1858 joules. The difference between these two units is beyond the limit of accuracy with which the mean calorie can be determined, the best estimates ranging from 4.1882 (Reynolds and Moorby) to 4.1925 (Dieterici). The quantity chiefly required in steam-engine work is the total heat  $h$  of the liquid under its own vapour pressure, and it is a matter of some convenience that the values of  $h$  at the fixed points  $0^{\circ}$  and  $100^{\circ}$  C. should be exactly 0 and 100 respectively.

**10. The Equation of Steady Flow.** One of the simplest illustrations of the law of conservation of energy, and one of the most important for the theory of steam, is the case of steady flow of a fluid. Suppose that steam or water or any other fluid enters an enclosure AB (Fig. 3) through the inlet A with constant velocity  $U_1$  at a constant pressure  $P_1$  and specific volume  $V_1$ , and leaves the enclosure at B with constant velocity  $U_2$ , at a constant pressure  $P_2$  and specific volume  $V_2$ . When the flow has become steady, it follows from the law of conservation of mass, that for each unit mass of fluid entering the enclosure at A, unit mass of fluid must in the same time leave the enclosure at B, provided that there is no leakage or other outlet. The enclosure AB may contain a throttle valve, or a porous plug, or an expanding nozzle, or a calorimeter,

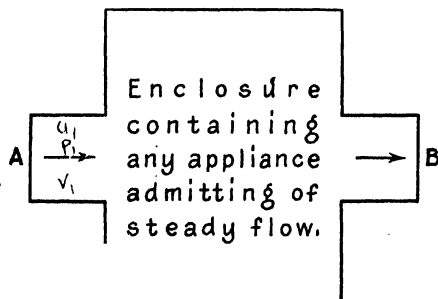


Fig. 3.

or a turbine, or any other appliance which admits of steady flow. It may even contain a reciprocating engine, provided that the dimensions of the receivers at the inlet and outlet are sufficient to render the flow practically uniform at these points.

The energy entering the enclosure at A with each unit mass of fluid, is the Total Energy per unit mass,  $E_1 + aP_1V_1 + AU_1^2/2g$ , consisting of the sum of the intrinsic energy  $E_1$ , the work  $aP_1V_1$ , and the kinetic energy  $AU_1^2/2g$ , in the initial state. The energy leaving the enclosure at B per unit mass is similarly the total energy  $E_2 + aP_2V_2 + AU_2^2/2g$  in the final state. By the law of the conservation of energy, the difference between the total energy entering and the total energy leaving the enclosure per unit mass, must be equal to the sum of the external loss of heat  $Q$ , measured per unit mass passing through, and the external work  $AW$  done

## 21] TOTAL HEAT OF WATER AND STEAM

by the appliance, measured in equivalent calories per unit mass. The complete equation may be written,

$$H_1 - H_2 = A (U_2^2 - U_1^2)/2g + Q_x + AW, \dots\dots\dots(2)$$

This includes a number of special cases which may be considered separately.

(1) *The Throttle.* If the appliance is a simple throttle valve, or porous plug, or small aperture, the function of which is simply to reduce the pressure, without any external work, or loss of heat, or increase of velocity, we may put the terms on the right hand side equal to zero, and we obtain the very simple and important result that the total heat remains constant, or  $H_1 = H_2$ . This is the essence of the "porous plug" method (Chapter III) devised by Joule and Thomson for investigating the variation of the total heat of a fluid.

(2) *The Nozzle.* The object of a nozzle, as employed in an impulse turbine, is to convert as much as possible of the energy into the kinetic form without external loss  $Q_x$  or work  $AW$ . Putting these two terms equal to zero, we obtain the condition

$$H_1 - H_2 = A (U_2^2 - U_1^2)/2g, \dots\dots\dots(3)$$

which shows that the kinetic energy generated is equal to the drop in total heat provided that there is no external loss. If there is friction, the drop in total heat is diminished, but the equation still holds. If eddies are formed, part of the kinetic energy will be unavailable. The flow must evidently be frictionless and linear to secure the maximum velocity. The maximum velocity obtainable under ideal conditions is given by the drop of total heat in "adiabatic" expansion, as will be explained later (Chapter VII).

(3) *The Turbine.* The object of the turbine is to obtain the maximum of external work  $AW$ , without heat loss  $Q_x$  or excessive waste in kinetic energy  $AU_2^2/2g$  of the steam rejected. If  $Q_x = 0$ , and  $U_2 = U_1$ , we obtain

$$H_1 - H_2 = AW, \dots\dots\dots(4)$$

which shows that the external work done is equal to the drop in total heat. The maximum drop of total heat obtainable under given conditions without external loss is that due to adiabatic expansion. There is necessarily a great deal of fluid friction and eddying motion in a turbine, which has the effect of reducing the drop of total heat to about  $\frac{2}{3}$  of the ideal maximum. But this effect is included in the equation, where  $H_1 - H_2$  represents the actual (and not the

adiabatic) value of the drop of total heat. There is generally some external loss  $Q_x$ , which must be subtracted from the heat-drop  $H_1 - H_2$  in estimating the actual output,  $W$  (Chapter XI).

(4) The reciprocating engine, with the limitation already implied, leads to the same law.

It will be observed that all the equations in which the work  $W$  is involved give no direct information with regard to the work obtainable. They simply assert that, if external work is done, there must be an equivalent drop of total heat, which is all that can be obtained from the law of conservation of energy. To find the limit obtainable it is always necessary to refer to Carnot's principle, as explained later (Chapter VII).

(5) *The Calorimeter.* The object of the calorimeter is to measure the change of total heat  $H_1 - H_2$  between given states by observing the quantity of heat  $Q$  per unit mass which must be abstracted to reduce the fluid from the first state to the second. The change of kinetic energy, and the work  $W$  are generally negligible, but can be allowed for if appreciable. The most convenient way of measuring  $Q_x$  is by observing the rise of temperature of a steady stream of cooling water.  $Q_x$  is often measured in this way in steady flow methods of calorimetry. It is also possible to reverse the process, and observe the increase of total heat produced by supplying energy with a stream of hot water, or an electric current, or a friction brake, or other means admitting accurate measurement. Other methods of calorimetry in which the flow is not steady, may generally be reduced to the equivalent case of steady flow, without material uncertainty as to the results. Two of the best examples are afforded by Regnault's measurements of the total heat of water and steam which he denoted by  $h$  and  $H$  respectively.

**11. The Total Heat of Water,  $h$ .** The intrinsic energy and total heat of water are generally reckoned from a zero corresponding to the state of water at the freezing point, because we are concerned only with changes of energy, and it is impossible to specify accurately the absolute value of the energy in any given state. Below  $100^\circ \text{C}$ . and atmospheric pressure, the changes of  $pv$  in the case of water are so small that it is seldom necessary to make any practical distinction between the intrinsic energy and total heat as already explained. Above  $100^\circ \text{C}$ . the distinction becomes more important as the pressure and volume increase, and it is necessary to consider the method of experiment employed, and the quantity actually measured.

Regnault operated by allowing 10 litres of water, under saturation pressure in a boiler at various temperatures between  $107^{\circ}$  and  $187^{\circ}$  C., to pass through a throttle-valve into a calorimeter containing 100 litres of water at atmospheric pressure and temperature. Passage through a throttle-valve does not alter the total heat, as we have already seen, provided that there is no external loss of heat and no change of kinetic energy. If kinetic energy is generated, it is reconverted into heat in the calorimeter. The result of Regnault's experiment is the same as if the water from the boiler, after passing the throttle, had a quantity of heat  $Q$  per unit mass abstracted from it, and were rejected at the final temperature of the calorimeter and atmospheric pressure. The quantity  $Q_2$ , estimated in the usual way from the thermal capacity and rise of temperature of the calorimeter, measures the change of total heat,  $h_1 - h_2$ , from boiler pressure and temperature to the final temperature of the calorimeter and atmospheric pressure. Unfortunately Regnault was ignorant of the variation of the specific heat of water at ordinary temperatures (subsequently discovered by Rowland), and of the temporary variations of zero of a mercury thermometer, which cannot be neglected in accurate calorimetric work. The first source of error can be corrected by reference to the original data with a fair degree of certainty, but the second only by estimation from the behaviour of similar mercury thermometers.

**12. Explanation of the Formula for  $h$ .** The formula employed for the heat of the liquid  $h$  in the author's original paper (*R. S.*, 1900) represented a combination of Regnault's results with those of the continuous electric method. It was shown, however, by MacFarlane Gray\* (*Proc. Inst. C. E.*, 1901-02, Part I, vol. 147, p. 8) that the results of the continuous electric method could be represented very closely above  $40^{\circ}$  C. by a thermodynamical formula,

$$h = st + aTv (dp/dT), \dots \dots \dots (5)$$

\* According to Gray (letter dated June 15, 1901) this formula was given by Paul de St Robert (*Thermodynamique*, Turin, 1857) as representing Regnault's heat of the liquid, but without any exact definition of the quantity denoted, which could in fact hardly have been expected at such an early date, when the function  $E + aPV$  was practically unknown, having been first applied by Joule and Thomson in their investigation of the equations of steady flow (*Proc. R. S.*, 1856). The simplicity and accuracy of all the derived relations given in this book depend primarily on the exact definition of the quantity denoted by the formula. On this point see also R. E. Baynes (*Science Abstracts*, 2059, Nov. 1902). After a long correspondence on the subject Gray refused to be converted to the author's definition of total heat and of the quantity denoted by  $h$  in the formula (5).

in which  $(dp/dT)$  represents the rate of increase of the saturation pressure  $p$  with temperature at  $T$ . Gray defined  $h$  in the same way as Regnault, and took the above expression as representing "the quantity of heat taken in by the liquid from 273 to  $T$ , the pressure during the heating being that due to the higher temperature."

In the revised equations (*E. B.*, 1902) the author adopted this expression, but with an essential change in the definition, as representing the thermodynamical total heat  $E + apv$  of the liquid under saturation pressure  $p$ . The total heat under this condition is greater than the quantity of heat involved in Gray's definition by the difference  $a(p - p_0)v_0$  approximately, which cannot be neglected in considering the properties of the liquid at high pressures. The advantage of this definition is that it greatly simplifies the relations between the volumes and total heats of the liquid and vapour, and gives a simple and exact expression for the entropy.

The formula for  $h$  was also interpreted as implying that the liquid contains in solution its own volume of the vapour, the latent heat of which contributes the term  $vL/(V - v)$  to the total heat of the liquid, where  $V$  is the volume of the dry saturated vapour (*Phil. Trans. A*, 1902, p. 147). If  $h$  is to be zero by definition at  $0^\circ\text{C}$ ., we require to add to the formula the small constant term  $-0.008$ , representing the value of  $vL/(V - v)$  at  $0^\circ\text{C}$ ., but this is so small that it may usually be neglected. We thus obtain the expressions

$$h = st + vL/(V - v) - 0.008 = st + (H - st)v/V - 0.008, \dots (6)$$

which are exactly consistent with Clapeyron's equation, namely

$$H - h = L = aT(V - v)(dp/dT), \dots (7)$$

and lead to the convenient relations

$$(h - st)/v = L/(V - v) = (H - st)/V, \dots (8)$$

which are much simpler than could be obtained by neglecting the variation of the specific heat of the liquid entirely, and are preferable to any of the purely empirical formulae commonly employed for the variation of  $h$ .

If the value of the constant  $s$  is determined by the condition that  $h$  is to be 100 mean calories at  $100^\circ\text{C}$ ., where the value of the term  $vL/(V - v)$  is 0.887 calorie, we obtain

$$s = 0.99666 = 1 - 1/800 \text{ nearly.} \dots (9)$$

The value of  $s$  found in this way is practically equal to that of the minimum specific heat at  $87.5^\circ\text{C}$ . indicated by the continuous

electric method, which is 0.9969 in terms of the mean specific heat between 0° and 100° C.

It will be observed that the formula does not pretend to represent the effect of the ice molecules in the liquid, which produce important effects on the variation of the specific heat in the neighbourhood of the freezing point. The maximum error from this cause is only a tenth of a calorie between 20° and 40° C., with smaller deviations at lower and higher temperatures. This is so unimportant in steam-engine work, where  $h$  is rarely required for small differences at low temperatures, that it was thought undesirable to complicate the formula by including a term to represent the ice molecules. In accurate calorimetry on the other hand, since the results depend chiefly on small differences of total heat in this region, it is essential to employ a formula which includes the effect of the ice molecules, such as that proposed by the author in a more recent paper (*Phil. Trans. A*, 212, p. 1, 1913).

**13. Comparison with Experiment.** The effect of the experimental evidence on which the formula is based, is most readily appreciated by plotting the value of the small difference  $h - t$  as in Fig. 4 (p. 32). Between 0° and 100° C. the difference is too small to be shown clearly on the scale of the diagram, and is quite unimportant in comparison with the uncertainty of the total heat  $H$  of steam. The formula is represented by the full curve above 100° C. in relation to the observations of Regnault and Dieterici, which are distinguished by + and × crosses respectively.

The observations of Regnault have been expressed in terms of the mean calorie by reference to the original calorimetric data, assuming the variation of specific heat given by the continuous electric method between 0° and 100° C. But they have not been corrected for errors of thermometry because any such correction would be highly speculative. Each point represents the mean of 5 to 10 experiments differing from the mean by two or three parts in 1000 in either direction. The results at 110° and 120° C. are evidently too high, and the general trend of the points plotted shows a systematic deviation from the formula which might easily be explained by thermometric errors. The experiments agree distinctly better with the author's definition of  $h$  than with Gray's, because the quantity actually measured by Regnault was the change of  $E + apv$ , as previously explained, and not the heat supplied at constant pressure  $p$ . If Gray's definition of the quantity



represented by the formula were adopted, it would be necessary to depress each of Regnault's points by the corresponding value of  $apv$ , shown in the lower curve, which would appreciably increase the discrepancy.

The observations of Dieterici (*Ann. Phys.* 16, p. 593, 1905) were not available at the time when the formula was published, but have the advantage of being comparatively free from thermometric uncertainties. He employed hermetically sealed bulbs of quartz-glass containing suitable quantities of water, which were heated to the required temperatures and dropped into a Bunsen ice-calorimeter at  $0^{\circ}$  C. The results which he gives are expressed in terms of the mean calorie, and represent the change of intrinsic energy  $E$  from  $0^{\circ}$  to  $t$  under saturation pressure. In order to deduce the corresponding values of  $h$  as represented by the formula, it is necessary to add the value of  $apv$  shown by the lower curve. This correction has been applied to the points as plotted, and brings them into very good agreement with the formula, except for one observation at  $156^{\circ}$ , which is evidently an experimental error. Dieterici continued the observations as far as  $300^{\circ}$  in spite of increasing difficulties, but the results at these temperatures are of little importance for steam-engine work, and are not shown in the figure. Up to  $240^{\circ}$  C. they agree very well with the formula. Beyond this point they fall slightly below it. This may indicate failure of the formula at high pressures, but it is equally likely that the difference is to be explained by experimental difficulties. Up to  $220^{\circ}$  C. the thermal capacity of the quartz-glass bulbs was about equal to that of the contained water. Beyond this point it was necessary to make the bulbs much thicker in order to withstand the pressure, and the thermal capacity of the bulbs was about four times that of the contained water, which would greatly increase the uncertainty of the results for the total heat of water.

Many steam tables (such as those of Mollier) still employ Regnault's formula for the total heat of water, namely

$$h = t + 0.00002t^2 + 0.0000008t^3, \dots\dots\dots(10)$$

with or without a reduction to the mean calorie. The values given by this formula when reduced to the mean calorie by dividing by 1.005, are shown by the dotted line in the figure. This line would represent Regnault's observations very fairly if they were all depressed by 0.5 calorie, which is the probable error at  $110^{\circ}$  C. But the empirical formula is not nearly so simple as the thermo-

dynamical formula, and disagrees materially with Dieterici's experiments. Many recent tables employ Dieterici's formula for the mean specific heat above  $100^{\circ}\text{C.}$ , but neglect the correction, *app.* His formula is of the same type as Regnault's and equally inconvenient in practice. It is obvious from the figure that the thermodynamical formula, with the author's interpretation, represents all the available experiments within the limits of probable error. It has accordingly been retained without modification, since it is greatly to be preferred for theoretical reasons. In any case the uncertainties of the total heat of the liquid are of very small practical importance as compared with those of the total heat of the vapour, which are shown on the same scale in the upper part of the same figure.

The thermodynamical basis of formula (5) is further explained in Chapter VIII, where its application is extended to the critical point.

**14. The Total Heat of Steam,  $H$ .** The total heat of dry saturated steam was defined and measured by Regnault\* as the quantity of heat required (1) to raise unit mass of the liquid from  $0^{\circ}\text{C.}$  to the temperature  $t$  of the boiler and (2) to evaporate it

\* In the author's original paper (*R. S.* 1900) all the expressions were worked out in terms of intrinsic energy  $E$  according to the usual custom in thermodynamics at that time. Regnault's definition was also adopted for the total heat  $H$  of saturated steam, for comparison with the values given by his experiments. The heat of the liquid  $h$  was taken from a formula which was assumed to represent the intrinsic energy. This afforded a perfectly consistent system which is still often adopted. The expressions given for  $H$  (as defined by Regnault) were necessarily less by the term  $a(p - p_0)b$  than the expressions given for  $H$  as now defined. The new definition of total heat as a name for the function  $E + aPV$  was first introduced in the revised expressions (*E. B.*, 1902), but the expressions for the intrinsic energy and entropy remain unaltered. The change of definition necessitated in the first instance the use of a different symbol  $F$  (*Phil. Mag.*, Jan. 1903) for the total heat  $E + apV$ , but the new definition has been adopted in the International Notation, and is now so well understood, that no confusion is likely to arise. Since everything required, including Regnault's heat of formation, can be more simply and accurately expressed in terms of  $H = E + aPV$  than in terms of Regnault's definition of  $H$ , it hardly seems necessary to retain his symbol in its original signification, which dates from a period before the first law of thermodynamics was formulated, and before the important properties of the function  $E + aPV$  were investigated by Rankine, and by Joule and Thomson (1854-1856). Mollier employs the symbol  $I$  for  $E + aPV$ , and calls it the total energy. He also uses Regnault's formula for  $h$  (giving  $h_{100} = 100.5$ ), which complicates many of the expressions unnecessarily, and introduces minor discrepancies in the calculations, especially in the deduction of the saturation pressure, and in the calculation of the entropy of the liquid by integrating  $(dh/dt)/T$  (see Chap. VII).

at that temperature, the whole operation being performed under constant pressure  $p$  equal to the saturation pressure at the temperature of the boiler. The heat of formation thus defined may be regarded as consisting of two parts. The second part is evidently the latent heat of vaporisation  $L$  at saturation pressure and temperature, about which there is no question. But the first part, the heat of the liquid, is the change of total heat  $h$  from  $0^\circ$  to  $t^\circ$  C. at constant pressure  $p$ , and differs slightly from the quantity actually measured by Regnault in his calorimetric experiments on the liquid. The difference amounts approximately to  $a(p - p_1)v_0$ , where  $v_0$  represents the volume of the liquid at  $0^\circ$  C. and atmospheric pressure  $p_1$ . The numerical value of the difference is zero at  $100^\circ$  C., and only 0.85 calorie at  $200^\circ$  C., which is much less than the probable error of Regnault's experiments and is quite unimportant in the case of steam. But it has given rise to some confusion, and the correction has often been applied with the wrong sign. The heat supplied to the liquid in the boiler at constant pressure  $p$  is less by the amount  $a(p - p_0)v_0$  approximately than the quantity which Regnault measured for the liquid and denoted by  $h$ . So that the total heat of steam, which Regnault measured by condensing steam in a calorimeter under a pressure equal to that of saturation maintained by an artificial atmosphere, would be equal, neglecting experimental errors, to

$$L + h - a(p - p_0)v_0.$$

The last term represents approximately the work done by the feed-pump in forcing the water into the boiler against the excess pressure  $p - p_0$ . This energy is not actually supplied as heat in this particular case, but should obviously be included in the total heat, which then reduces to  $L + h$ .

If on the other hand the total heat of dry saturated steam was measured in the same way as Regnault measured that of water, namely by passage through a throttle and condensation at atmospheric pressure (which has been done by Willans and others), the quantity measured (when corrected to zero) would be simply  $L + h$ , which is the quantity really required. More generally this method gives the change of total heat  $H$ , defined as the thermodynamic function  $E + aPV$ , from steam to water at atmospheric pressure, whatever be the initial state of the steam with regard to temperature, pressure, superheat or wetness. The name Total Heat appears particularly appropriate on this account, because the

change of  $H$  is the total quantity of heat actually measured under experimental conditions.

**15. Regnault's Experiments on  $H$  and  $L$ .** Regnault represented the results of his experiments on the total heat of saturated steam between  $0^\circ$  and  $200^\circ$  C. by the simple linear formula,

$$H = 606.5 + 0.805t, \dots\dots\dots(11)$$

which was universally adopted for more than fifty years, and gives in reality a very fair value of the mean rate of variation between  $100^\circ$  and  $200^\circ$  C., where his experiments were most concordant. That this formula did not represent the variation below  $100^\circ$  C. (which is most important in these days of turbines) in an equally satisfactory manner, was first shown by the experiments of Dieterici (*Wied. Ann.* 37, p. 506, 1889) at  $0^\circ$  C., and of E. H. Griffiths (*Phil. Trans. A*, 186, p. 261, 1895) at  $30^\circ$  and  $40^\circ$  C. These observations have been confirmed by all subsequent work, and there is no doubt at the present time that Regnault's formula is insufficiently accurate in this region as well as theoretically inadmissible.

In order to appreciate the value of the experimental evidence, the results of Regnault and subsequent observers are plotted in Fig. 4 on the same scale as that already employed for the total heat of water. Since the object of the figure is to bring out clearly the differences between various methods, the difference of each result from the value given by Regnault's formula at the same temperature is the quantity plotted in the figure. Regnault's formula is represented by the horizontal straight line marked O. Observations giving a lower result than Regnault's formula lie below the line, those giving higher results above. The differences are plotted in mean calories Centigrade. The actual observations recorded by Regnault himself are shown by the plain circles, each of which represents the mean of several experiments under similar conditions. The crossed circles represent results of subsequent observers. The plain circle giving the value 636.7, or 0.8 calorie less than Regnault's formula, at  $100^\circ$  C., represents the mean of 38 experiments giving 636.7 for the total heat at atmospheric pressure; or 536.2 calories for the latent heat at  $100^\circ$  C., if Regnault's formula is adopted for the total heat of the liquid. Regnault was well aware that this result was probably too low on account of the presence of a small proportion of water in the steam, but he was unable to eliminate this source of error completely. The four plain circles between  $65^\circ$  and  $85^\circ$  C. represent the results of 22 experi-

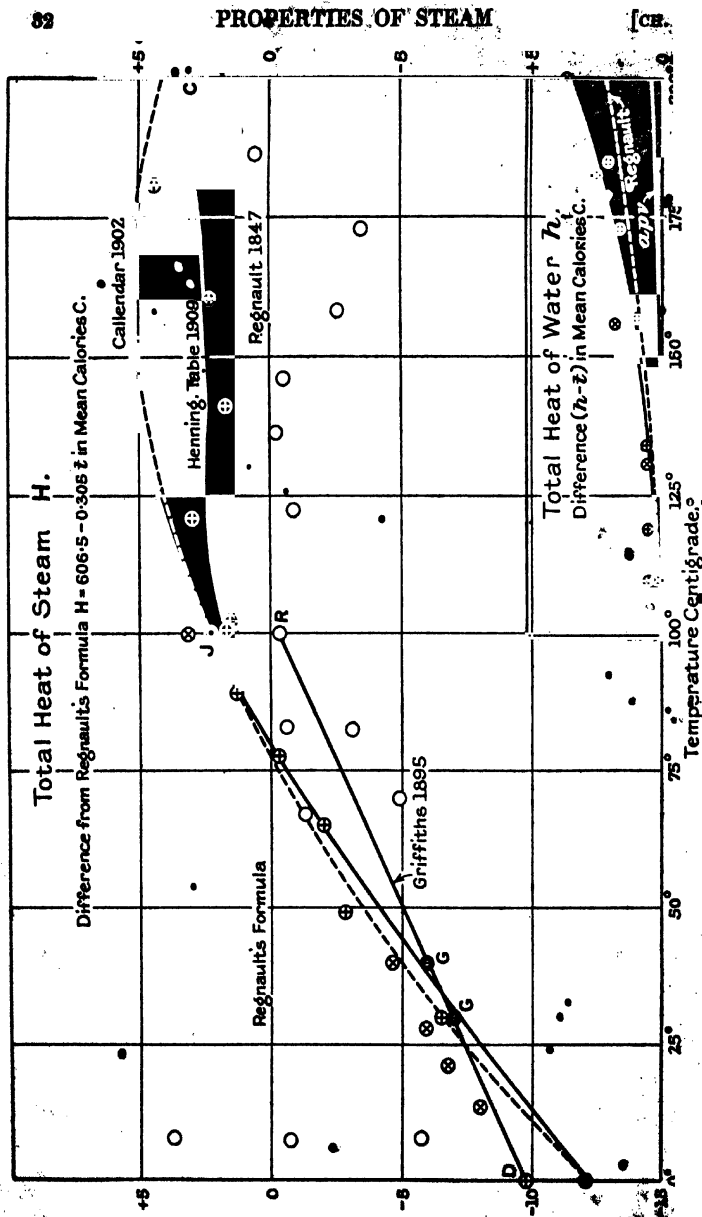


Fig. 4. Total Heat of Water and Steam.

ments in four groups, some of which nearly reach the line, while others lie 5 or 6 calories below. The mean of all shows a defect from the formula of 2.5 calories, or 0.4 per cent. of the total heat at 75° C. Combining the mean of these with the observation at 100° C. we should obtain a rate of increase of 0.40 in place of 0.30 for the total heat between 75° and 100° C., as remarked by Griffiths.

Regnault's observations are liable to another source of error which has not previously been noticed. The calorimeter gains heat by conduction through the pipe by which the steam is admitted. Regnault estimated this gain by observing the rise of temperature of an exactly similar calorimeter, with similar connections, to which no steam was admitted. He assumed that the gain of heat by conduction through the connecting pipe would be the same for the calorimeter in which the steam was condensed as for the idle calorimeter, since both were connected to the same distributing tap at the temperature of the steam. This assumption is evidently unsound, because the flow of steam would necessarily reduce the temperature gradient in the connecting pipe, on which the flow of heat by conduction depends. He made a similar error in his experiments on the specific heats of gases. The effect of overestimating the correction in this manner was to make his results too low.

In the experiments above 100° C. the possibilities of error from leakage increased rapidly with increase of pressure. Great trouble was experienced from this cause and the effects of leakage became very obtrusive when the pressure reached 10 atmospheres. The joints had to be renewed daily, and many other precautions taken which had previously been neglected. It would appear that errors from leakage were largely responsible for the low points between 150° and 175° C., since Regnault gave no weight to these points in selecting his formula.

The three sources of error above mentioned would all tend to make the results too low by an uncertain amount for which no correction can now be applied. The observations are also affected by the calorimetric errors previously mentioned in the case of the liquid, for which some appropriate correction might be estimated. But these corrections are so small in comparison with the uncertain sources of error that it has not been thought necessary to make any reductions of this kind in the case of steam.

Regnault's observations between - 2° and 16° C., the means of which in three groups are indicated by the plain circles in the neighbourhood of 8° C., were obtained with a different method and

apparatus under conditions most unfavourable to accuracy. The results of experiments under similar conditions varied by 10 or 15 calories, and though the mean of all agreed fairly with his formula, it is plain that Regnault himself attached little weight to this series of observations.

**16. Dieterici, Griffiths and Joly.** Dieterici (*loc. cit.* 1889) measured the latent heat at  $0^{\circ}\text{C}$ . by evaporating a known weight of water in a Bunsen ice calorimeter and observing the weight of mercury extruded. The observations were very concordant, seldom differing by more than one calorie from the mean value 596.8, which is indicated in the figure by the point marked D at  $0^{\circ}\text{C}$ . The weakest point of the determination was that he assumed the constant of the ice calorimeter to be 15.44 milligrams of mercury per mean calorie from the mean of the results of previous observers.

Griffiths (*loc. cit.* 1895) measured the latent heat of evaporation by observing the supply of electrical energy required to keep the temperature of his calorimeter constant while a known weight of water was being evaporated. He at first employed a current of air for evaporating the liquid, but finally succeeded in obtaining much better results by evaporating the water drop by drop under its own vapour pressure from an accurately weighed tube. His results for the latent heat in terms of the calorie at  $15^{\circ}\text{C}$ . were 578.7 at  $30.0^{\circ}$ , and 572.6 at  $40.15^{\circ}\text{C}$ . He observed that these two results lay very nearly on the straight line, DGR in Fig. 4, joining Dieterici's value at  $0^{\circ}\text{C}$ . and Regnault's value at  $100^{\circ}\text{C}$ ., so that the variation of the total heat between these limits could be represented with considerable accuracy by a linear formula with a coefficient 0.40 in place of Regnault's 0.305, provided that Dieterici's calorie and Regnault's unit were both equal to the calorie at  $15^{\circ}\text{C}$ .

In order to test the possibility of this assumption, Griffiths persuaded Joly to make a determination of the relation between the latent heat of condensation at  $100^{\circ}\text{C}$ . and the mean specific heat of water from  $12^{\circ}$  to  $100^{\circ}\text{C}$ . with the Joly steam calorimeter which was admirably adapted for the purpose. The results of ten closely concordant experiments gave the mean specific heat from  $11.89^{\circ}$  to  $99.96^{\circ}\text{C}$ . as 0.9952, if the latent heat at  $99.96^{\circ}\text{C}$ . were assumed to be 586.66. This showed either that the mean thermal unit must be much smaller than the calorie at  $15^{\circ}\text{C}$ ., or that Regnault's value of the total heat at  $100^{\circ}\text{C}$ . was too low. The latter supposition was the more probable, because Joly's method was

free from nearly all the uncertain errors already enumerated in the case of Regnault's method.

A satisfactory comparison between these important results first became possible in the course of the preliminary reduction of the observations on the variation of the specific heat of water between 0° and 100° C. by the continuous electric method (*Brit. Assoc. Rep.* 1899) which showed (1) that Griffiths' unit was in fact very nearly equal to the mean calorie, as he had supposed, and (2) that the value of the latent heat at 100° C. deduced from Joly's experiments should be 539.8 in terms of the same unit. The points marked G and J are plotted on this assumption in Fig. 4.

The continuous curve marked GJC passing through these points and extending from 0° to 200° C. represents the theoretical curve of variation of the total heat of steam deduced from measurements of the specific heat and the cooling effect as described in the next chapter. This curve agreed very well with Joly and Griffiths, but appeared to indicate that all Regnault's results between 100° and 200° C. were too low. It was impossible to escape from this conclusion if the results of Joly and Griffiths were admitted, because it was obvious that the curve of variation must be continuous, and the agreement with Joly and Griffiths below 100° C. afforded very strong evidence in favour of the theoretical curve at higher temperatures.

Dieterici's value at 0° C., though agreeing far better with the theoretical curve than Regnault's value, could not be brought into exact agreement with it unless the constant of the ice calorimeter were 15.50 in place of 15.44 mgm. per calorie as assumed by Dieterici. The constant was subsequently redetermined by Dieterici with great care in 1905 (*loc. cit.* p. 603). He found the value 15.491, which has recently been confirmed by E. Griffiths (*Proc. Phys. Soc.* 26, p. 1, 1913), who found 15.486 for 4.184 joules, or 15.498 per mean calorie of 4.187 joules as here employed. The corrected result obtained by employing this value of the constant is distinguished by a double circle which falls very nearly on the theoretical curve at 0° C.

The equation of the theoretical curve for dry saturated steam at a pressure  $p$  is as follows:

$$H = 0.4772T - SCp + 464 \text{ calories C. ....(12)}$$

where  $S$  is the specific heat at  $p$ , and  $C$  the Joule-Thomson cooling-effect



**17. Results of Later Observers.** Subsequent observations of the latent heat have tended to confirm the conclusions thus reached. Henning (*Ann. Phys.* 21, p. 849, 1906) obtained values of the latent heat at six points between 30° and 100° C. by a modification of Griffiths' method, suggested by Ramsay and Marshall's experiments (*Phil. Mag.* 41, p. 38, 1896). His results are expressed in terms of the calorie at 15° C. which he takes as equivalent to 4.188 joules from the observations of Jacger and Steinwehr (*Zeit. Instr.* 25, p. 104, 1905) with similar Weston cells. His results are indicated by circles enclosing ( + ) crosses at 30.1, 49.1, 64.9, 77.3, 89.3, and 100.6° C. Each point represents the mean of a number of observations, which are not quite so consistent as those of Griffiths, because the external loss of heat was not so perfectly compensated. Three of the points lie practically on the curve, but the two at 30° and 49° are appreciably higher, while that at 100° is slightly lower.

A. W. Smith (*Phys. Rev.* 25, p. 145, 1907), employing a current of air for evaporation, expressed his results for the latent heat in joules per gram, assuming the electromotive force of the Weston cell to be 1.01888 volts at 20° C. His values are reduced to the same unit as that here employed by taking the electromotive force of the Weston cell to be 1.0183 volts, and the mean calorie to be 4.187 joules\*. His observations are indicated in the figure by the circles

\* There is necessarily some uncertainty in reducing results, such as those of Smith, expressed in terms of the electrical units. Fortunately Griffiths' results, though obtained by electrical methods, were directly referred to the calorie at 15° C., the absolute values of his electrical standards and of the mechanical equivalent of heat being immaterial for the purpose of reduction (Griffiths, *loc. cit.*, p. 272). Dieterici also determined the constant of his ice-calorimeter directly by means of water at 100° C., so that his results can be corrected with a fair degree of certainty to mean calories, since no electrical measurements were involved. Henning's results, as given in terms of the calorie at 15° C., were similarly independent of any assumption with regard to the electromotive force of the cells employed, because the same cells were employed in the determination of the equivalent factor for reduction. Henning (*Ann. Phys.*, 29, p. 444, 1909) complains with apparent reason that Smith reduced his results incorrectly. Smith also reduced the results of Griffiths and Dieterici to joules, for comparison with his own observations, by making certain assumptions with regard to the electrical units. These reductions brought the results of Dieterici, Griffiths, and Henning, into very good agreement with Smith's, but involve material errors and uncertainties. Unfortunately Davis and other writers have accepted Smith's reductions implicitly. Thus Dieterici's result, expressed in mean calories and corrected for the constant of his ice-calorimeter, after conversion into joules by one factor and reconversion back into calories by another, is brought nearly into agreement with his original uncorrected value! Griffiths' and Henning's results are similarly raised from their original values in terms of the calorie at 15° C.,

with diagonal ( $\times$ ) crosses, at 14.0, 21.2, 28.1, and 39.8° C. They are seen to be systematically higher than those of Griffiths and Henning, but agree closely with Dieterici's uncorrected result. At a later date (*Phys. Rev.* 33, p. 181) Smith took some observations at 100° C. The point shown at 100° C. with a diagonal cross is one which Smith obtained by *slow* evaporation, and is nearly 1 calorie higher than Joly's observation. He obtained much lower values by rapid boiling, which he explained by supposing that water was carried over in minute quantity with the steam, a very probable source of error in such cases. He considers that the highest values merit the greatest confidence on this account. There is a good deal of truth in this, especially at high temperatures on account of the density of the vapour, but the discrepancy affects all Smith's observations to a similar extent, and might easily be explained by other causes. In any case it would not materially affect the *form* of the curve of variation.

Henning (*Ann. Phys.* 29, p. 441, 1909) subsequently made a series of observations of the latent heat at 5 points between 100° and 180° C., the results of which are indicated in the figure by (+) crosses. The values of the total heat are deduced from those of the latent heat by adding the total heat of the liquid obtained from Dieterici's formula, which is in practical agreement with that employed by the author, and cannot introduce any material discrepancy. The results are too discordant to be represented by any reasonable formula, but confirm the conclusion that Regnault's observations in this region were considerably too low. The wavy line marked "Henning's Table" represents his table of the probable values of the total heat, which has commonly been adopted by subsequent writers. But this curve was deduced by a graphic process of smoothing and does not represent the actual observations satisfactorily. It is obviously inadmissible for theoretical purposes, as it involves a discontinuity in the curve at 100° C. and would necessarily introduce inconsistencies in all the thermodynamical relations. Three of the five observations are in very fair  
whereas they should have been slightly lowered in reduction to mean calories, because the calorie at 15° C. is about 1 in 2000 less than the mean calorie. All unnecessary reductions of this kind are strongly to be deprecated. It has seemed better in the present work not to apply any reductions to the work of other observers when the correction is small as compared with the uncertainty of measurement. It is well to bear in mind such corrections when comparing observations or choosing a formula. But they may prove very confusing to subsequent computers who are not familiar with all the conditions assumed in the reductions, and have frequently resulted in material errors of the kind described.

agreement with the author's theoretical curve, but the other two are lower by about 0.5 per cent., which is quite a possible error in such difficult experiments, and is less than the differences between the individual observations at each point.

The method of deducing the variation of the total heat from observations of the specific heat and the cooling effect, as explained in the next chapter, has the great advantage that the observations are comparatively simple, and that errors from wetness, or leakage, or loss of heat, are easily eliminated. Moreover, the whole variation between 100° and 180° C. is less than one-twentieth part of the total heat, so that an error of 1 per cent. in the specific heat, or in the cooling effect, would produce an error of less than a twentieth of 1 per cent. in the value of the total heat at 180° reckoned from 100° C. The results prove conclusively that the true values of the total heat at 140° and 160° C. cannot possibly be so low as Henning's observations at these points would appear to indicate. Although no satisfactory observations of the specific heat or the cooling effect are at present available at pressures above 10 atmospheres, it seems justifiable to extrapolate the saturation curve to 200° C., and to give greater weight to Henning's observation at 180° C. than he does himself on account of its close agreement with the theoretical curve.

**18. Empirical Formulae for  $H$ , and  $L$ .** Since Regnault's linear formula for the total heat of steam was shown to be unsatisfactory, many attempts have been made to construct more suitable empirical formulae to represent the observations. The most obvious type to select is a parabolic formula such as that proposed by Ekholm (*Fort. Phys.* 46, II, p. 371),

$$H = 596.75 + 0.4401t - 0.000634t^2 \dots\dots\dots (18)$$

Regnault calculated many similar formulae to represent his observations on other vapours. It is very easy to calculate a formula of this type to represent any selected values of the total heat of steam over a limited range. But such a formula has no theoretical significance, and cannot be trusted for extrapolation. A formula capable of extrapolation is particularly desirable in the case of steam, because the direct observations are numerous and fairly concordant between 0° and 100° C., but the observations at higher temperatures are comparatively few, and rapidly become uncertain and discordant with increase of pressure.

Of empirical formulæ hitherto proposed for the latent heat, the most suitable type for extrapolation is that of Thiesen (*Verh. Deut. Phys. Ges.* 16, p. 80, 1897), which has been found to suit a great variety of cases. It is based on the generally accepted view that the latent heat must vanish at the critical temperature  $t_c$ , and was originally given in the form

$$L = L_1 (t_c - t)^{\frac{1}{2}}, \dots\dots\dots(14)$$

where  $L_1$  is a constant representing the value of  $L$  when  $t_c \div t = 1$ , and the index  $\frac{1}{2}$  was at first assumed to be the same for all substances. It appears necessary, however, to admit slight variations in the value of the index for different substances.

In the case of steam, Henning represented his observations below 100° C. by a formula of this type, namely,

$$L = 94.210 (365 - t)^{0.31248}, \dots\dots\dots(15)$$

in which the critical temperature is assumed to be 365° C. Davis and Jakob in reducing results of experiments on the specific heat above 100° C. employed a similar formula, namely,

$$L = 92.93 (365 - t)^{0.3150}, \dots\dots\dots(16)$$

A formula of this type has generally been adopted by other computers for the purpose of extrapolation. It is essential, however, if the formula is to have any weight for this purpose, to employ the correct value of the critical temperature, which makes a very considerable difference in the results.

Traube and Teichner (*Ann. Phys.* 13, p. 620, 1904), by the meniscus method, found the critical point of water to be 374° C. This observation is easily verified with a silica tube, and there is no doubt that their figure is a close approximation to the true critical temperature. If this value is inserted in the above formulæ, keeping the index and the value of  $L$  at 100° C. the same, and putting the expression in the logarithmic form, as required for practical calculation, we obtain, for Henning's formula,

$$\log L = 1.96955 + 0.81248 \log (374 - t), \dots\dots\dots(17)$$

Similarly with the formula employed by Davis and Jakob, if we keep the same value of the index, but alter  $t_c$  to 374, and take  $L = 589.8$  at 100° C., we obtain

$$\log L = 1.96898 + 0.8150 \log (374 - t), \dots\dots\dots(18)$$

If on the other hand we take the same value of  $L$  at  $100^{\circ}\text{C.}$ , but calculate the value of the index to make  $L = 594.3$  at  $0^{\circ}\text{C.}$ , we obtain

$$\log L = 1.97145 + 0.31192 \log (874 - t) \dots\dots (19)$$

The values given by these formulae are collected in the following table for comparison with those given by Henning and Jakob.

Table I. Values of  $L$  by Formulae of the Thiesen type.

Temp. Cent.	HENNING $k=0.3125$		DAVIS AND JAKOB $k=0.3150$		AUTHOR $k=0.3119$	
	$t_c=365$	$t_c=374$	$t_c=365$	$t_c=374$	$t_c=374$	Theoretical formula
$0^{\circ}$	595.4	593.7	596.1	594.8	594.3	594.3
$20^{\circ}$	585.1	583.6	585.6	584.6	584.2	583.8
$40^{\circ}$	574.3	573.1	574.7	574.0	573.7	573.2
$60^{\circ}$	562.9	562.2	563.3	562.9	562.7	562.3
$80^{\circ}$	551.1	550.7	551.4	551.4	551.3	551.1
$100^{\circ}$	538.7	538.7	538.9	539.3	539.3	539.3
$120^{\circ}$	525.7	526.1	525.7	526.6	526.7	526.9
$140^{\circ}$	511.9	512.8	511.8	513.2	513.4	513.6
$160^{\circ}$	497.2	498.7	497.0	498.9	499.3	499.3
$180^{\circ}$	481.5	483.6	481.2	483.7	484.2	483.9
$200^{\circ}$	464.6	467.4	464.1	467.4	468.1	467.4

All the formulae agree in giving higher values than Henning's table between  $120^{\circ}$  and  $160^{\circ}\text{C.}$  even when  $365^{\circ}$  is taken for  $t_c$ . The substitution of the correct value of the critical temperature raises the values by about 3 calories at  $200^{\circ}$  in each case, and brings them into close agreement with the author's theoretical formula. It also improves the agreement with the observations of Griffiths and Dieterici, especially the latter, if the point at  $100^{\circ}$  is raised to 589.3.

The employment of the erroneous value  $365^{\circ}$  for the critical temperature appears to have led computers, who have commonly employed this formula for extrapolation, to raise all the values of  $H$  and  $L$  unduly at low temperatures, and to depress them excessively at  $200^{\circ}\text{C.}$ , against the weight of experimental evidence. If the correct value of the critical temperature had been recognised sooner, it is probable that more weight would have been attached to Henning's value at  $180^{\circ}\text{C.}$ , and it would have been admitted that Regnault's values at  $190^{\circ}\text{C.}$  were probably still too low like his values at  $100^{\circ}\text{C.}$  Thiesen's formula undoubtedly gives some useful indication of the values of the latent heat to be expected.

between  $100^{\circ}$  and the critical temperature. At the same time it must be remembered that it is merely an empirical formula, without thermodynamical foundation apart from the vanishing of the latent heat at the critical temperature. The dotted curve shown in Fig. 4 represents the values of the total heat obtained from the formula for the latent heat shown in the last column but one of the table, calculated from the observations of Dieterici and Joly at  $0^{\circ}$  and  $100^{\circ}$  C. This curve agrees with the full curve representing the theoretical formula within 1 in 1000, intersecting the author's curve at  $160^{\circ}$  and again at  $260^{\circ}$  C. Between these two points, it lies a little above the author's, and it is very likely that it gives too high results at  $200^{\circ}$  and above, though the index is very nearly the same as Henning's. The index 0.3150 employed by Davis and Jakob gives exact agreement with the author's values at  $100^{\circ}$  and  $200^{\circ}$ , if the critical temperature is  $374^{\circ}$ , and it is to be preferred for extrapolation, above  $200^{\circ}$  C. It agrees with the theoretical formula within less than 1 in 1000 from  $100^{\circ}$  to  $200^{\circ}$ , and within 1 in 5000 from  $200^{\circ}$  to  $230^{\circ}$  (where the agreement is again exact), and the difference is still very small at  $250^{\circ}$  C. The author's formula for the total heat, which applies to dry steam in any state, superheated or supersaturated, and is in many ways simpler and more convenient than Thiesen's, has accordingly been extrapolated in the tables to  $259^{\circ}$  C. Although the direct experimental evidence does not extend beyond  $180^{\circ}$  C., it seems reasonable to infer that the values are sufficiently accurate for practical purposes at higher temperatures, because the calculated values of the saturation pressure (which depend on small differences and afford a very severe test of the theory) also agree with observation to within less than  $1^{\circ}$  C. at  $250^{\circ}$  C. The values of the saturation-volume, in so far as they depend on  $dp/dt$ , are much less certain than those of the total heat, but are probably as accurate as any that can be obtained by experiment at these pressures. In any case they are exactly consistent with the adiabatic equation and other formulae, and will serve as a useful guide for theoretical extensions.

## CHAPTER III

### THE JOULE-THOMSON METHOD

**19: Origin of the Present Theory.** Since the measurement of the specific heat of steam, and the application of the Joule-Thomson method to deduce the variation of the total heat, formed the starting point of the present theory, the conclusions will be rendered more intelligible if some account is here given of the steps by which they were reached.

It was early remarked by Rankine (1850), and subsequently by Kirchhoff (1858), that the coefficient 0.305 in Regnault's formula for the total heat of saturated steam, ought to be equal to the specific heat  $S$  at constant pressure, if steam obeyed the laws of an ideal gas with constant specific heat, for which

$$aPV = RT, \text{ and } E + aPV = ST + B, \dots\dots\dots(1)$$

where  $R$ ,  $S$ , and  $B$  are constants. The specific heat  $S$  of superheated steam was measured shortly afterwards by Regnault at atmospheric pressure over the range  $124^{\circ}$  to  $222^{\circ}$  C., and found to be 0.48, which greatly exceeded the value 0.305 required by the formula for the total heat on the ideal-gas theory. The experimental value,  $S = 0.48$ , was generally accepted, and the discrepancy explained by supposing, as Kirchhoff suggested, that steam at low pressures departed widely from the ordinary gas laws. Some writers, however, held that the value 0.48 was probably in error, because the quantity of heat corresponding to the superheat of the steam from  $124^{\circ}$  to  $222^{\circ}$  C., namely 47 calories, on which the experimental value of  $S$  depended, was only a small fraction of the total heat, about 700 calories, measured in condensing the superheated steam in the calorimeter. But this objection would apply with even greater force to the value of the constant 0.305 in the formula for the total heat of saturated steam obtained by condensing steam at widely different pressures.

One of the most consistent views was that held by Osborne Reynolds and Perry (*Steam-Engine*, 1899, p. 582) who considered that the specific heat should approximate to 0.305 at low pressures

and temperatures, but increased considerably with temperature, rising to a mean value in the neighbourhood of 0.48 over the range 124° to 222° C. This view received some support from a calculation made by MacFarlane Gray on the basis of Regnault's experiments. He noticed that if the specific heat were calculated from the 16 experiments at 128.7° C. giving 645.63 as the mean value of the total heat at this point at atmospheric pressure, assuming  $H = 686.68$  at 100° C., the value of  $S$  obtained, namely  $8.95/23.7$ , or 0.378, was intermediate between 0.305 and 0.48. Gray himself believed that the specific heat was constant and equal to 0.385 (as calculated previously by Rankine on the assumption that the ratio of the specific heats was 1.40), and explained the difference between Regnault's experimental values, 0.38 and 0.48, over different ranges, by supposing that "any particles of moisture in the steam at 100° C. would not be evaporated up to 124° C.; but they would be more likely to be evaporated in the higher range of temperature." Zeuner, on the other hand (*Zcit. Ver. Deut. Ing.* xi, p. 41, 1867), succeeded in fitting the value  $S = 0.48$  with other properties of saturated steam by admitting large deviations from the ideal state at low pressures, and considered that  $S$  should be independent of the pressure in accordance with his well known equation for the volume (Chap. IV, equation (1)). It will be seen that the state of uncertainty with regard to the actual value of the specific heat of steam was most unsatisfactory about this time, and that it was a matter of some practical importance to make further appeals to experiment by new methods.

**20. The Throttling Calorimeter.** Joule and Thomson were the first to explain how it was that saturated steam became dried and superheated by throttling to lower pressures, but they do not appear to have made any measurements for steam. The first application of their method to steam seems to have been made by Peabody (*Thermodynamics of the Steam Engine*, p. 237) in the use of the "Throttling Calorimeter" for determining the wetness fraction  $J' - q$ . According to Regnault's formula, the total heat  $H'$  of wet steam at  $t'$  is

$$H' = 637 + 0.805 (t' - 100) - (1 - q) L', \dots\dots\dots(2)$$

where  $L'$  is the latent heat at  $t'$ . If the steam is throttled to atmospheric pressure, the total heat remains the same (provided that there is no loss or gain of heat or kinetic energy) and is given in



terms of the mean specific heat  $S$  at atmospheric pressure by the expression

$$H' = 687 + S(t'' - 100), \dots\dots\dots(3)$$

where  $t''$  is the observed temperature of the throttled steam. Equating the two values of the total heat, we obtain a formula for the wetness fraction

$$(1 - q)L' = 0.805(t' - 100) - S(t'' - 100) \dots\dots\dots(4)$$

The method is very delicate, because an increase of 1 per cent. in the wetness of the initial steam lowers the temperature  $t''$  observed after throttling by about  $10^\circ$  C. Ewing and Dunkerley (*B. A. Report*, 1897, p. 354) applied this method to find the value of  $S$  in terms of Regnault's coefficient 0.805 for the variation of total heat of dry saturated steam. They took the steam as directly as possible from a separator to the calorimeter, and calculated  $S$ , assuming  $q = 1$ , by means of the formula

$$S = 0.805(t' - 100)/(t'' - 100). \dots\dots\dots(5)$$

In this way they found values of  $S$  intermediate between 0.805 and 0.48, but no details were given in the report.

A very complete investigation, founded on the same principle, was made in the laboratory of Osborne Reynolds by J. H. Grindley (*Phil. Trans. A*, 1900, p. 1), who found values of  $S$  ranging from 0.887 at  $100^\circ$ , to 0.665 at  $160^\circ$  C. These experiments were of great value, and will be more fully discussed in a later section, but they left the true value of  $S$  more uncertain than ever.

Prof. J. T. Nicolson and the author in their experiments "On the Law of Condensation of Steam" (*Proc. Inst. C. E.*, 1898), employed a throttling calorimeter of the type shown in Fig. 5, connected to a large vertical steam-pipe supplying the engine. The steam-pipe could be made to act as a fairly efficient separator by turning the entrance nozzle as indicated in the figure. The steam was throttled through a thin tube of small bore, in order to eliminate the error due to conduction of heat through the throttle, to which most forms of throttling calorimeter then in vogue were liable. After circulating round the thermometer pocket, the throttled steam, before leaving the apparatus, was made to circulate twice round the calorimeter to minimise external loss. The whole apparatus, including the steam-pipe and the throttle tube, was well lagged in the usual way. The pressure after passing the throttle was generally atmospheric, but an exit throttle and gauge were provided

for raising the pressure and observing its value when required. The exit could also be connected, if desired, to a condenser vacuum, or to a surface condenser at atmospheric pressure, when it was required to measure the quantity of steam passed. Provision was also made for readily changing the throttle tube, to suit different initial pressures.

The wetness fractions determined with this apparatus, employing formula (4) with Regnault's coefficients, persisted in coming out negative (which was obviously impossible), in spite of all precautions which experience in calorimetry could suggest. This showed either

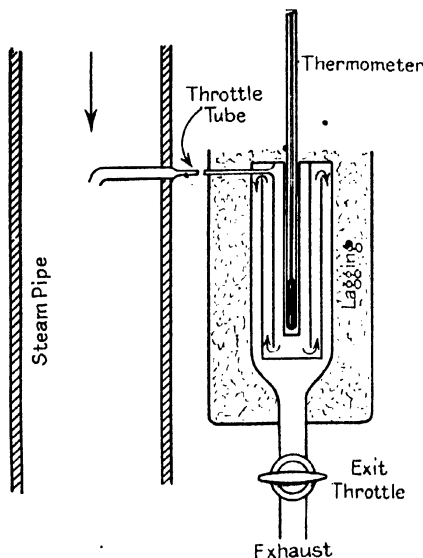


Fig. 5. Single Throttling Calorimeter.

that Regnault's value of  $S$  was too high at temperatures near  $100^{\circ}\text{C.}$ , as many had already suggested, or else that his value of the coefficient 0.805 for the variation of the total heat was too low in the same region, and should be more nearly 0.40, as Griffiths (*loc. cit.* 1895) had proposed as the result of his experiments on the latent heat.

**21. Experiments on the Specific Heat of Steam.** It was accordingly decided to make a direct determination of the specific

heat at atmospheric pressure by the continuous electric method, which had been devised some years previously for the determination of the mechanical equivalent, and which had already been brought to a fairly high degree of accuracy by investigating the various sources of error incidental to the method. A steady current of steam at atmospheric pressure, superheated by throttling in the manner already described, was passed through a tube, suitably jacketed externally and containing an electric heating coil. The electric energy supplied was measured by means of Weston instruments, calibrated by the potentiometer method. The rise of temperature, due to the watts supplied, was observed by a pile of several thermo-junctions in series, standardised by comparison with a platinum resistance thermometer. The external loss was eliminated by taking two sets of observations at the same rise of temperature with different currents of steam, the current of steam in each case being measured by condensation in a surface condenser. The results obtained for  $S$  showed discrepancies of 1 or 2 per cent. as was to be expected from the comparative roughness of the method of measurement and the difficulty of keeping the steam current perfectly steady, but indicated a value of the specific heat falling from 0.50 to 0.49 over the range of temperature from 110° to 160° covered by the experiments. This was regarded as a decisive confirmation of Regnault's value over the higher range, and as showing that the limiting value of the specific heat at zero pressure was probably nearly constant, as in the case of many other gases.

**22. Variation of the Total Heat.** Having thus obtained by direct experiment the values of the specific heat at atmospheric pressure over the required range of temperature, it was possible to deduce the variation of the total heat of dry saturated steam at temperatures above 100° C., from the observations already taken with the throttling calorimeter, by means of the equation

$$H_t - H_{100} = S(t'' - 100), \dots\dots\dots(6)$$

where  $H_t$  is the total heat of dry saturated steam at the initial temperature and pressure, and  $S$  is the mean specific heat at atmospheric pressure from 100° C. to  $t''$ , the temperature observed after throttling to atmospheric pressure. The curve of variation of total heat found in this way was shown in Fig. 4, p. 32, instead of being straight like Regnault's, with a constant coefficient

$dH/dT = 0.805$ , showed a decided curvature, the rate of increase falling from 0.40 calorie/1° at 100° C. to 0.80 at 160° C. This indicated that Regnault's coefficient 0.305 might be a fair average over the range 100° to 200° C., where his experiments were most concordant, but that the coefficient probably increased at low temperatures, approximating to the value 0.475 (as it should according to Rankine's theory) at low pressures, where the vapour should behave nearly as a perfect gas. This view, while disagreeing materially with Kirchhoff's, and with Regnault's observations of  $\bar{H}$  at low temperatures, gave good agreement with the experiments of Dieterici at 0° C., and of Griffiths at 30° and 40° C., but the curve could not be fitted with either if Regnault's value at 100° C. was adopted. Fortunately Joly's observation at 100° C., when reduced on the highly probable assumption (since verified by the results of the continuous electric method), that the mean specific heat of water from 0° to 100° C. was nearly equal to that at 15° C., served to bridge the gap by indicating that Regnault's value at 100° C. was probably 2 or 3 calories too low. These results agreed in showing that the coefficient  $dH/dT$  for saturated steam was not constant and equal to 0.305, but diminished from 0.48 at low pressures, to 0.40 at 100° C., and about 0.22 at 200° C., in consequence of the increasing deviation of the volume of the vapour from the ideal value with increase of pressure. This diminution of  $dH/dT$  was clearly necessitated by the existence of the Joule-Thomson cooling effect, which also required a corresponding variation of the specific heat with pressure. This is easily seen by considering the relation between the specific heat, the cooling-effect, and the variation of the total heat.

**23. The Cooling-Effect,  $C$ .** The cooling-effect  $C$  is defined as the ratio of the fall of temperature to the fall of pressure in a throttling process at constant total heat. It is a coefficient of equal importance in theory to the specific heat, but has the advantage in practice of being more easily measured, since no measurements of heat quantities are required.

To illustrate the relation of  $C$  to  $S$  and  $dH/dT$ , we may refer to the annexed figure, drawn to scale, which shows a portion of the saturation line AC on the  $p, t$  diagram giving the pressure  $p$  of saturated steam in lbs. per sq. in. for temperatures  $t$  between 140° and 160° C. If dry steam is taken off at any point A, say at 80 lbs. and 155.5° C., and is throttled to a lower pressure, say 60 lbs.,

the state of the steam after throttling will be represented by the point B at  $151^{\circ}\text{C}$ . The temperature at this point is lower by the difference  $BD = 4.5^{\circ}\text{C}$ . than the initial temperature at A, but the total heat  $H$  is the same at B as at A. The line AB represents a line of constant total heat on the  $p, t$  diagram. The cooling-effect  $C$  is the slope of such a line at any point, and is measured by the ratio  $BD/AD$  of the drop of temperature  $dt$  to the drop of pressure  $dp$ , which is commonly denoted by the differential coefficient  $(dt/dp)_H$ , where the suffix  $H$  indicates that the ratio of  $dt$  to  $dp$  is taken under the condition of constant  $H$ . Since the lines of constant  $H$  are nearly straight, the numerical value of  $C$ , namely  $4.5/20$ , or  $0.225^{\circ}/\text{lb.}$ ,

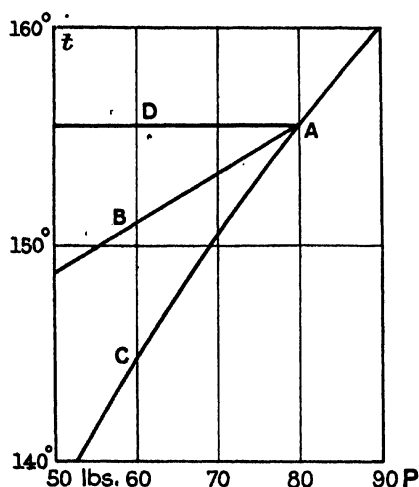


Fig. 6. Cooling-Effect on  $p, t$  Diagram.

found in this way over a finite range, may be taken as representing very nearly the slope of the curve AB at the middle point of the range, namely at  $70\text{ lbs.}$  and  $158.2^{\circ}\text{C}$ . The cooling-effect  $C$  has a positive sign when a drop of temperature accompanies a drop of pressure, as is usually the case in dealing with vapours.

Since the total heat at A is the same as that at B, the drop of total heat  $dH$  from A to C along the saturation curve is the same as the drop of  $H$  from B to C, namely the product  $S \times BC$  of the specific heat  $S$  at  $60\text{ lbs.}$  and the drop of temperature  $BC$ , since  $BC$  is a line of constant pressure. The drop of total heat *per degree fall* along the saturation curve, denoted by  $(dH/dT)_s$ , is therefore

equal to  $S \times BC/DC$ , since  $DC$  is the drop of  $t$  corresponding to the drop of  $H$ , between  $A$  and  $C$ . In other words  $(dH/dT)_s$  must be less than  $S$  in the ratio  $BC/DC$ . The temperature at the point  $C$ , taken from the tables at 60 lbs., is  $144.8^\circ \text{C}$ . Hence •

$$DC = 155.5 - 144.8 = 10.7^\circ \text{C}.$$

But  $BC = DC - DB = 10.7 - 4.5 = 6.2^\circ \text{C}.$

So that the ratio  $BC/DC = 6.2/10.7 = 0.58$  at this point; or the rate of increase of  $H$ , with temperature is little more than half the value of  $S$ . But the value of  $S$  at 60 lbs. near the saturation line is not quite the same as at atmospheric pressure.

It is easy to put the relation in a more general form in terms of known coefficients. Since  $DB = C \times DA$ , by the definition of  $C$ , and since  $DA/DC$  is the ratio of the drop of pressure to the drop of temperature (or the familiar coefficient  $dp/dt$ ) along the saturation line, the ratio  $BC/DC$  is  $1 - C(dp/dt)$ , or

$$(dH/dT)_s = S(1 - Cdp/dt). \dots\dots\dots(7)$$

This well known relation is mathematically exact in the limit for small differences of  $p$  and  $t$ , being in fact simply the general expression for the variation of  $H$  in terms of  $S$  and  $C$ , applied to the saturation line (Appendix I (15)). It shows that the rate of increase of  $H$ , will be practically equal to  $S$  at  $0^\circ \text{C}$ . (since  $dp/dt$  is very small), but must diminish rapidly at high pressures since  $dp/dt$  increases much faster than  $C$  diminishes with rise of temperature. It is also clear that  $(dH/dT)_s$  must vanish, or the total heat of saturated steam must reach a maximum, when  $Cdp/dt = 1$ , or when the line of constant total heat becomes tangential to the saturation line on the  $p, t$  diagram. Beyond this point saturated steam would increase in wetness, instead of being dried, by throttling. But this point is beyond the range of any existing experiments on  $C$ , or  $S$ , or  $H$ .

In applying mathematical relations of this kind to the results of experiment, we are often met by the difficulty that the coefficients required, such as  $S$  and  $C$  and  $dp/dt$ , have to be measured over finite ranges of temperature, as in the foregoing numerical example, and that the values so found will not be quite exact when applied to points indefinitely close to the saturation line, where they cannot actually be measured. The only satisfactory way of meeting this difficulty is to frame a simple theory of the relation of the coefficients concerned. Any such theory must be exactly consistent

with the laws of thermodynamics, and must at the same time represent the actual variation of the coefficients within the limits of accuracy of experimental measurement.

**24. The Joule-Thomson Equation.** The experimental methods of determining  $S$  and  $C$  depend essentially on observing variations of  $H$ , but it is most important that the expressions chosen to represent the results of such experiments, especially the variation of  $C$  with temperature, should be thermodynamically consistent with the variations of the volume  $V$ , the next most important quantity required in practical thermodynamics. This agreement is readily tested by means of the second law of thermodynamics (Appendix I (39)), which gives the relation

$$SC = aT (dV/dT)_P - aV. \dots\dots\dots(8)$$

This important relation was first given by Joule and Thomson in a different form (*Phil. Trans.*, 1854, p. 355), but they reduced it at a later date (*Phil. Trans.*, 1862, p. 587) to the above shape which is most convenient for the purpose.

Joule and Thomson found as the result of their experiments on air and  $\text{CO}_2$ , that the cooling-effect in both cases was independent of the pressure, but diminished rapidly with rise of temperature. The diminution of  $C$  with rise of temperature might have been represented by a great variety of empirical formulae\*; but they adopted the expression  $C = K/T^2$ , because it gave a solution of the thermodynamical relation (8) agreeing closely with an equation which Rankine (*Phil. Trans.*, 1854, p. 337) had deduced from Regnault's experiments on the deviation of the volume of  $\text{CO}_2$  from the ideal value. By integrating equation (8) on the assumption that  $S$  was constant, and that  $V$  must approximate indefinitely to  $RT/P$  at high temperatures, Joule and Thomson obtained their well known form of characteristic equation for  $V$  in terms of  $T$  and  $P$ , namely,

$$aV = RT/P - KS/3T^2. \dots\dots\dots(9)$$

The original equation of Joule and Thomson was liable to the objection that it did not represent the result which they observed in the case of hydrogen, namely a rise of temperature with fall of pressure (or a negative value of  $C$ ), which increased instead of

\* Other writers have in fact suggested different formulae for  $C$ , some of which fit the actual observations of  $C$  better, but give absurd results for  $V$ . It is therefore most important to select a suitable type of formula (*Phil. Mag.*, Jan. 1903).

diminishing when the temperature was raised. It appears probable that, at sufficiently high temperatures, all other gases would behave in the same way as hydrogen does at ordinary temperatures. This is most readily included in the formula by putting  $V - b$  in place of  $V$  in the left hand side of (9), where  $b$  is a small constant representing the limiting volume beyond which the gas cannot be compressed however great the pressure. The introduction of  $b$  into the equation considerably improves the agreement at high pressures.

The method of integration, assuming  $S$  constant, is obviously inadmissible if  $S$  is really variable. We find in fact that the original equation of Joule and Thomson does not represent the properties of  $\text{CO}_2$  quite satisfactorily with the value of  $K$  deduced from the observations on the cooling-effect. The agreement is greatly improved if account is taken of the known variation of  $S$  with temperature. The easiest way to do this (*Phil. Mag.*, Jan. 1903, p. 75) is to proceed in the inverse order if the variation of  $S$  is known. Assume an equation of the type

$$V - b = RT/aP - K/T^n, \dots\dots\dots(10)$$

and deduce the values of  $K$  and  $n$  by comparing the experiments on  $S$  and  $C$  with the resulting expression for  $SC$  by relation (8), namely,

$$SC = a(n + 1) K/T^n - ab. \dots\dots\dots(11)$$

In the case of steam it was evident from the magnitude of the cooling effect, and its rapid variation with temperature, that there must be a considerable variation of  $S$  with pressure, according to the thermodynamic relation, which follows from the first law (Appendix I (35)),

$$(dS/dP)_t = - (dSC/dT)_p. \dots\dots\dots(12)$$

The large variation of  $S$  with pressure, while not at all affecting the previous deduction of  $H_g$  from equation (6) by the throttling method, for which the value of  $S$  at atmospheric pressure alone was required, raised a fresh difficulty in another quarter. It appeared at first sight to be inconsistent with some previous experiments on the adiabatic expansion of steam, which required a constant value of the index representing the ratio of the specific heats. The solution of this difficulty was not immediately obvious, but it ultimately led to a considerable simplification of the expressions for the various properties of steam.



**25. The Adiabatic Equation for Dry Steam.** In the experiments on the Law of Condensation of Steam at McGill College in 1895, a large number of observations of the temperature of steam under various conditions in the cylinder of a steam-engine had been taken by means of a delicate platinum thermometer, constructed of wire .001" in diameter, which was sufficiently sensitive to measure the temperature of the steam to about  $0.1^{\circ}\text{C}$ . under favourable conditions with the engine running at 100 revs. per min. In most cases the temperature found was simply that of saturation corresponding to the pressure shown by the indicator. But when the steam was dry, the relation between pressure and temperature was that given by the adiabatic law,  $P/T^{n+1} = \text{constant}$ . The index of  $T$  in this equation is the ratio  $S/R$  in the case of a perfect gas, and is constant if  $S$  is constant. Contrary to expecta-

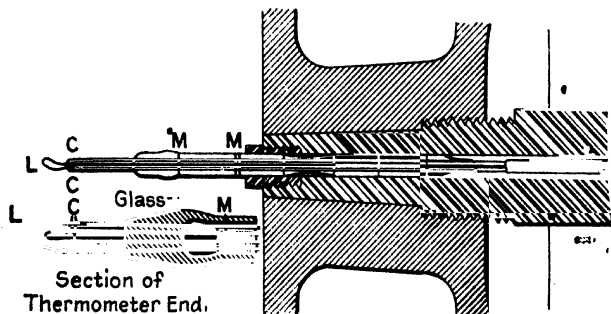


Fig. 7. Piston Thermometer.

tion, the value of the index  $n + 1$  was found to be remarkably constant for steam, and to be very little affected by condensation on the walls, or by leakage, or by variation of pressure. Leakage and condensation would both very seriously affect the value of the index deduced from the curves shown on the indicator card, represented by  $P^n V^{n+1} = \text{constant}$ , since the mass would not remain constant. But neither condensation nor leakage had much effect on the pressure-temperature relation, because the thermometer showed the temperature in the middle of the cylinder where the change was practically adiabatic. The constancy of the index was tested by a special series of observations, in which the ports of the cylinder were blocked with lead to prevent leakage, while the cylinder was heated with steam in the jacket and steam-chest. Under these conditions it was possible to test the law over a wide

range of pressure and temperature. The value of  $n + 1$  found in this way for steam was  $13/8$ , or  $4.33$ . Observations were also taken with air in the cylinder under the same conditions as a check on the performance of the thermometer, because the adiabatic law was known for air with a fair degree of certainty. The thermometer was automatically compensated for conduction along the leads by connecting a short loop of the same .001" wire to the ends of the compensating leads, as shown in the annexed Fig. 7. The radiation error was checked by the experiments on air, and found to be very small if the wire was clean. The method, though at first sight so unpromising, proved to be the most accurate (as is now generally recognised), for measuring the adiabatic index.

**26. General Type of Characteristic Equation.** The result that the index  $n + 1$  was constant for steam and equal to  $13/8$ , fitted extremely well with the view that  $S$  was constant and equal to  $0.477$ , because the value of  $R$  for steam is  $.1101$ , and the ratio  $S/R$  is  $4.33$ . But it was not at first sight obvious how the index could be independent of the pressure for an imperfect vapour, when it was found that  $S$  varied so widely with pressure. It was shown, however, by theoretical investigation, that this property would be possessed by any vapour, however imperfect, provided that its intrinsic energy  $E$  could be represented by the expression

$$E = anP(V - b) + B, \dots\dots\dots(13)^*$$

where  $b$  and  $B$  are constants. It was also found that the characteristic equation of the vapour must be of the general type

$$aP(V - b)/T = F(P/T^{n+1}), \dots\dots\dots(14)$$

where  $F$  represents any arbitrary function of the argument  $(P/T^{n+1})$ , which remains constant in adiabatic expansion. The perfect

\* If  $E = anP(V - b) + B$ , and  $H = a(n + 1)P(V - b) + abP + B$ , it follows that the specific heats at constant pressure,  $S_p$ , and at constant volume,  $S_v$ , are

$$S_p = a(n + 1)P(dV/dT)_p, \text{ and } S_v = an(V - b)(dP/dT)_v. \dots\dots\dots(15)$$

But the difference  $S_p - S_v$  is given by the well known expression (Appendix I, (48)),

$$S_p - S_v = aT(dP/dT)_v(dV/dT)_p. \dots\dots\dots(17)$$

We thus obtain a simple differential equation for  $T$ , namely,

$$T = (n + 1)P(dT/dP)_v - \frac{b}{V} (V - b)(dT/dV)_p, \dots\dots\dots(18)$$

the general solution of which is (14), as given in the text. The solution may be put in a great variety of forms, since it involves an arbitrary function, but the special

gas is a special case in which the function  $F$  is constant and equal to  $R$ , but this does not satisfy the other conditions of the problem. The solution next in simplicity of a suitable type is obtained by taking

$$aP(V - b)/T = R + KP/T^{n+1}, \dots\dots\dots (15)$$

where  $R$  is the constant to which  $aP(V - b)/T$  approximates when  $P$  is small, and  $K$  is another constant to be determined by observing the deviations from the ideal state as the pressure increases. It was impracticable in the case of steam to follow the methods adopted in the case of gases, of observing the deviations from Boyle's law, or the coefficient of expansion and the pressure-coefficient. Attempts had been made in this direction, but showed little promise of leading to results of sufficient accuracy. It was obvious from the measurements already made that the cooling-effect  $C$  was roughly independent of the pressure, as Joule and Thomson had found, but their method of integration, assuming  $S$  constant, was inadequate in the case of such large variations of specific heat as had been indicated in the case of steam. It was accordingly decided to repeat the throttling experiments with additional precautions in order to test the possibility of this solution, and if found satisfactory, to deduce the value of the constant  $K$ .

**27. The Differential Throttling Calorimeter.** The single throttling calorimeter previously employed was well adapted

form (15), given in the text, is the most convenient for the purpose for which it is required.

Further, since the general expression (App. I (40)), for heat received,  $dQ$ , is

$$dQ = S_p dT - aT (dV/dT)_p dP, \dots\dots\dots (16)$$

it follows by substituting the above value (16) for  $S_p$ , that when  $dQ=0$ , in an adiabatic process, we must have

$$dP/P = (n+1) dT/T, \text{ which gives } P/T^{n+1} = \text{constant.} \dots\dots\dots (20)$$

By expressing  $dQ$  in terms of  $S_p$ , we similarly obtain  $(V - b) T^n = \text{constant}$ , or by combining the two,  $P(V - b)/T = \text{constant}$ , for the adiabatic equation.

These thermodynamical relations are more fully discussed and explained in Appendix I.

Since the general expression for the variation of  $H$  is, App. I (14),

$$dH = SdT - SCdP,$$

the assumption that  $SC$  is a function of the temperature only, agreeing with equation (15) or (21), gives a much simpler expression for  $H$ , namely equation (24), than the assumption that  $C$  is a function of the temperature only, as made by Joule and Thomson, which is inconsistent with their assumption  $S$  constant, and leads to a different type of characteristic equation, as shown in the next chapter, § 30.

or obtaining the differences of  $H$ , over a considerable range (as from saturation to atmospheric pressure), required in the previous experiments, but it was not so well adapted for obtaining values of the cooling-effect  $C$  at a particular point. The value of  $C$  at a particular temperature and pressure could be obtained only by successive observations (during which the state of the initial steam might vary), or by differentiating the curves of constant total heat. Since a change of 1 per cent. in the wetness of the steam produced a change of about  $10^{\circ}\text{C}$ . in the temperature observed after throttling, it was most important to employ a differential method in which such

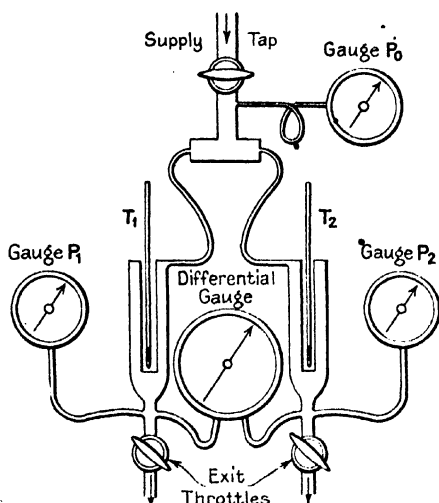


Fig. 8. Differential Throttling Calorimeter.

changes were automatically eliminated. This was effected by connecting two exactly similar calorimeters (Fig. 8) to the same steam supply, and adjusting the terminal pressures  $p'$  and  $p''$  by independent valves to a suitable difference  $p' - p''$  read on a differential gauge. The corresponding difference of temperature  $t' - t''$  was read with a differential pair of platinum thermometers. From which the value of the cooling-effect  $C = (t' - t'')/(p' - p'')$  at the mean pressure and temperature is directly obtained, with almost complete elimination of errors due to variation of wetness or external loss of heat. The calorimeters were made of thin steel

tube, and each was well lagged and drained, and doubly jacketed with its own exhaust, so that a steady state was reached in about 5 minutes after turning on the steam. This apparatus was completed early in July 1897, and was exhibited to several members of the British Association on the occasion of their visit to McGill College, but, owing to pressure of other work, the observations taken with it could not be reduced in time for the meeting at Toronto. These were supplemented by some taken by the fourth year students during the following session, and showed that the proposed form of characteristic equation (15) afforded a satisfactory solution of the difficulty\*.

**28. The Coaggregation Volume  $c$ .** For moderate ranges of pressure, such as are commonly required in practice, the relation between the pressure, volume, and temperature of a gas or vapour may most conveniently be written in the form

$$V - b = RT/aP - c. \dots\dots\dots(21)$$

The constant  $R$  is the limiting value of the ratio  $aPV/T$  in mean

\* The main results of these experiments were included in the original paper (*Proc. R. S.*, 87, p. 268, 1900, referred to by the abbreviation (*R. S.*, 1900) in this work), but the details of the observations and apparatus were reserved for later communications, referred to (*loc. cit.*, p. 268) as "the papers which follow" on the "Differential Throttling Calorimeter," and on the "Electrical Method of Measuring the Specific Heat of Steam." These two papers were not published in the *Proceedings of the Royal Society* as originally intended, because Prof. Nicolson was then making preparations to repeat the throttling experiments on a more extended scale at Manchester, and did not wish the details published immediately. He also intended to work out a new set of Steam Tables based on the author's equations, but was ultimately compelled by ill health and overwork to abandon both of these intentions. The experiments on the specific heat of steam and air were described, and the apparatus exhibited, at meetings of the Physical Society of London in Oct. and Nov. 1902, as recorded in the Minutes of Proceedings for those dates; but the papers themselves were not published *in extenso*, because the author, as Honorary Treasurer of the Society, did not feel justified in asking the Society to print such long and elaborate communications, the essential results of which had already been published elsewhere. These papers described additional experiments by improved methods, and confirmed the original results, giving 13/3 for the adiabatic index, or the ratio  $S_p/R$ , which was accordingly adopted, in place of Maxwell's theoretical value 4.5, in the revised equations for steam, published in the *Encyclopaedia Britannica*, 1902, vol. 33, articles Thermodynamics and Vaporisation, which are referred to in this work by the abbreviation (*E. B.*, 1902). This modification was found to give improved agreement with experiment for all the properties of steam, but without affecting the theory or the general character of the conclusions. Some further details, with diagrams of the original apparatus, have since been given in the preface to a paper by J. H. Brinkworth, B.Sc., "On the Specific Heat of Steam," *Phil. Trans. R. S.*, Series A, vol. 215, p. 383. Confirmatory results for the ratio  $S_p/R$  were obtained by Makower, and given in the *Phil. Mag.*, Feb. 1903, p. 226.

calories per degree when the pressure is small. It has the value 0.11012 if the index  $n$  is taken as 10/3, and the value of the specific heat  $S_0$  at zero pressure is taken as 0.47719. These values agree sufficiently well with the experiments on the specific heat and the adiabatic index, and also with the conventional values of the atomic weights. It is important for convenience of calculation that  $n$  should be a simple fraction, and that the ratio  $S_0/R$  should be exactly equal to  $n + 1$ , but the absolute values cannot be determined by experiment closer than 1 in 1000. The values of the constants  $R$  and  $S_0$  when expressed in mean thermal units per unit mass per degree are the same in all systems of units, but the reduction factor  $a$  is different in different systems (Chapter II, § 8).

The small quantity  $b$  is often called the "covolume" or the "molecular volume." It is here assumed to represent the volume occupied by unit mass of the substance when the molecules are practically in contact, as in the liquid state. It is so small in comparison with  $V$  that it cannot be determined with accuracy by experiments on the vapour, except in the case of non-condensable gases at very high pressures. It is therefore taken in the case of water as being equal to the volume of the liquid at 0° C. We thus obtain

$$b = 1 \text{ cu. cm. per gram, or } 0.01602 \text{ cu. ft. per lb.}$$

The small quantity  $c$  is called the "coaggregation volume," and expresses the diminution of volume produced by coaggregation or pairing of molecules. As already explained, the simplest expression that can be selected for  $c$  is

$$c = c_1 (T_1/T)^n,$$

where  $c_1$  is the value of  $c$  at some standard temperature  $T_1$ , preferably 100° C. or 373.1° abs. The value of  $c_1$  remains to be determined from the observations on the cooling-effect  $C$ , which also serves as a subsidiary verification of the value of  $n$ .

The coaggregation volume  $c$  affords a very convenient method of expressing the deviations of all the properties of the vapour from the state of ideal gas, representing the limiting state of the vapour at zero pressure. All the experiments hitherto made on gases and vapours tend to confirm the conclusion that the defect of volume  $c - b$  from the ideal volume  $RT/aP$  is a function of the temperature only to a first approximation at low pressures, and can be represented for a fairly extended range of temperature by supposing  $c$  to vary inversely as some power  $n$  of  $T$ , where  $n$  may

have different values for molecules of different types. There is no great difficulty in calculating the deviations from the ideal state in terms of  $c$  for other assumptions with regard to the variation of  $c$ , but the assumption  $c = c_1 (T_1/T)^n$  suffices for most practical purposes, and gives the following simple expressions:

Defect of Volume, $V$ ,	$= c - b$ .
Defect of Energy, $E$ ,	$= ancP$ .
Defect of Entropy, $\Phi$ ,	$= ancP/T$ .
Defect of Total Heat, $H$ ,	$= (a(n+1)c - ab)P$ ,
Value of $SC$	$= a(n+1)c - ab$ .
Value of $S - S_0$	$= an(n+1)cP/T$ .
Increment of $G = T\Phi - H$ ,	$= a(c - b)P$ .
Increment of $\log_e p$ ,	$= a(c - b)P/RT$ .

These give very simple thermodynamical relations between the various properties, and are greatly to be preferred to any of the purely empirical formulæ commonly employed. The two last are of special simplicity and importance, since they are independent of the assumption that  $c$  varies as  $T^{-n}$ , and remain true for any variation of  $c$  provided that it is a function of the temperature only. The saturation pressure  $p$  of the vapour differs from that of an ideal gas by a factor depending only on the ratio of the defect of volume to the ideal volume. If  $c - b$  is not a function of the temperature only, the increment of  $G$  is represented by the integral of  $a(c - b) dP$  at constant  $T$ , which is readily determined on any desired hypothesis, but no satisfactory law of variation of  $c$  or  $b$  at high pressures has yet been discovered.

In the case of steam we have the additional simplification that the ratio  $S_0/R$  is equal to  $n + 1$ , to a close approximation, which has the effect of reducing the equation of the adiabatic to the same form as for an ideal gas, as already explained. This is so great an advantage, that, even if it were not so accurately true as it appears to be, it would still be most useful in practice.

**29. Expressions for  $E, H, C$  and  $S$ .** Since the form of the characteristic equation has been chosen to satisfy the condition, found experimentally, that the index  $(n + 1)$  is constant in the adiabatic expansion of dry steam, it follows that the Intrinsic Energy  $E$  can be represented by the extremely simple expression, previously given,

$$E = anP(c - b) + B, \dots\dots\dots(18)$$

where  $B = 464.00$  mean calories Centigrade if  $E$  is reckoned from

the state of water at 0° C. This expression is perfectly general for dry steam, whether superheated or supersaturated, and includes the intermediate case of saturated steam.

The corresponding expression for the Total Heat  $H$  is obtained by simply adding  $aPV$  to the expression for  $E$ , since  $H = E + aPV$ ,

$$H = a(n+1)P(V-b) + abP + B. \dots\dots(22)$$

This equation, when inverted, gives a very useful expression for  $V$  in terms of  $H$  and  $P$ , namely,

$$V = 3(H-B)/13aP + 10b/13. \dots\dots\dots(23)$$

The numerical values of the constants in different systems of units are given in the Steam Tables, Appendix III, § 191.

Both  $E$  and  $H$  are readily expressed in terms of  $P$  and  $T$ , by substituting  $V-b = RT/aP - c$ , from the characteristic equation, thus,

$$\begin{aligned} E &= nRT - ancP + B, \\ H &= (n+1)RT - a(n+1)cP + abP + B. \end{aligned}$$

This equation may also be written in the form

$$H = S_0T - SCP + B, \dots\dots\dots(24)$$

where  $SC$  represents the product of the specific heat  $S$  and the cooling-effect  $C$  at a temperature  $T$  and pressure  $P$ .  $S_0$  is the limiting value of  $S$  at zero pressure, which is taken as constant and equal to  $(n+1)R$ .

The values of  $H$  for dry saturated steam are obtained by substituting for  $P$  the value of the saturation pressure  $p$  corresponding to the temperature, together with the appropriate value of  $c$ . The values thus obtained for  $H_s$  are represented by the curve in Fig. 4, and have already been verified by comparison with direct experiments on the total and latent heats. It might be supposed at first sight that the formula for  $H_s$ , since it involves  $p$  as well as  $T$ , is unnecessarily complicated, as compared with empirical formulae giving  $H_s$  directly as a function of  $T$ . But it is more convenient in practice to retain  $p$  explicitly in the formula, since the saturation value of  $H$  is merely a special case of the general expression, and  $p$  is always known.

The general expression for the specific heat  $S$  at constant pressure, namely  $(dH/dT)_p$ , is immediately obtained by differentiating the expression for  $H$  with regard to  $T$  under the condition



$P = \text{constant}$ . Remembering that  $c = c_1 (T_1/T)^n$ , we observe that  $(dc/dT) = -nc/T$ . Whence

$$S = (dH/dT)_{P_0} = (n+1)R + an(n+1)cP/T = S_0 + an(n+1)cP/T. \quad \dots\dots\dots(25)$$

The limiting value of the specific heat  $S_0$  at zero pressure must be constant and equal to  $(n+1)R$ , if  $n$  is constant. The small term involving  $c$  expresses the complete variation with pressure at different temperatures. It will be seen that this term remains constant, when  $P/T^{n+1}$  is constant, in adiabatic expansion.

The value of  $(dH/dP)$  when  $T$  is constant, is equal to  $-SC$ , by the definition of the cooling-effect  $C$ . Differentiating the expression for  $H$  with regard to  $P$  at constant temperature, we obtain the equation for  $SC$ ,

$$SC = -(dH/dP)_T = a(n+1)c - ab. \quad \dots\dots\dots(26)$$

This equation shows that the cooling-effect  $C$  should not be quite independent of the pressure at constant temperature, but should diminish slightly as  $P$  increases in consequence of the increase of  $S$  with pressure. The value of  $c$  may be deduced from this equation if  $C$  is known for any given  $P$  and  $T$ .

**30. Relation between  $C$  and  $c$ .** Substituting for  $S$  its value in terms of  $c$ , the last equation (26) may be employed to find  $C$  in terms of  $c$  or *vice versa*.

$$c = (RC/a + b/(n+1))/(1 - nCP/T), \quad \dots\dots\dots(27)$$

$$C = (c - b/(n+1))/(R/a + ncP/T). \quad \dots\dots\dots(28)$$

Since  $b/(n+1)$  is very small,  $C$  is very nearly proportional to  $c$  at low pressures, so that both may be taken to vary inversely as the same power  $n$  of the temperature  $T$  to a close approximation. For the same reason, the ratio of  $C$  to  $c$  is nearly constant along an adiabatic at all pressures, since  $ncP/T$  is constant. The constant  $b/(n+1)$  is .0087 cu. ft./lb. which is less than 1 per cent. of  $c$  at 100° C. The constant  $R/a$  is the same as that in the equation for the volume  $V$ , and has the value 1.07061 when  $P$  is in lbs./sq. in. and  $V$  in cu. ft. per lb. Thus the cooling-effect  $C$  in °C. per lb. pressure is of nearly the same order of numerical magnitude as  $c$  measured in cu. ft./lb., namely  $C = 0.871^\circ \text{C. per lb. at 1 atmosphere and } 100^\circ \text{C. where } c = 0.518 \text{ cu. ft. per lb.}$

The values of  $C$  obtained with the differential throttling calori-

meter were employed to calculate corresponding values of  $c$  at the mean points of each experiment. The values deduced for the constant  $c_1$  at  $100^\circ \text{C}$ . agreed very closely when calculated from those of  $c$  at different pressures and temperatures, showing that the adiabatic index correctly expressed the variation with temperature. The agreement was not quite so good with  $n = 3.5$  for the index, but was almost within the limits of error of experiment. The value given for the constant  $c_1$  with the index  $n = 3.5$  in the original paper (*R. S.* 1900) was 26.50 cu. cms. per gm. at  $100^\circ \text{C}$ . This was reduced to 26.80 by changing the index to  $n = 10/3$ . The change is small, because, as already remarked, the ratio  $c/C$  is nearly independent of  $n$  at low pressures. The value of  $c$  at  $160^\circ \text{C}$ . was increased by nearly the same amount, the value at  $130^\circ \text{C}$ . remaining unchanged. The corresponding value at  $100^\circ \text{C}$ . when expressed in cubic feet per pound, or in cubic metres per kilo as employed in practice, is

$$c_1 \text{ (at } 100^\circ \text{C.)} = 0.4213 \text{ cu. ft./lb.} = 0.02680 \text{ cu. m./kg.}$$

The coaggregation volume  $c$ , being a function of the temperature only, is very easily calculated and tabulated.\* The same remark applies to the simple functions  $SC = a(n+1)c - ab$ , and  $Z = anc/T$ , which are required for the total heat and cooling-effect, and for the entropy and specific heat respectively. These are included in Table I, Steam Tables, Appendix I.

## CHAPTER IV

### THE COOLING-EFFECT $C$

**31. Experimental Values of  $C$  by the Differential Method.** The following are some of the values of the cooling-effect  $C$  observed with the differential throttling calorimeter by Prof. Nicolson and the author in July, and by the fourth year students at McGill College during the winter session of 1897. Each value represents the mean of ten readings of the temperature and pressure differences. Most of the observations were taken between  $150^{\circ}$  and  $120^{\circ}$ , and between 15 and 50 lbs. pressure. It was more difficult to get observations at higher temperatures and pressures. Those given in the table have been selected so as to cover the experimental range as evenly as possible.

Table I. Observations of the Cooling-Effect  $C$ .

$t_m$	$P_m$	$t' - t''$	$P' - P''$	$C$	$c$ (obs.)	$c$ (calc.)
179.2	120.4	2.33	13.3	0.175	0.224	0.222
175.3	94.5	3.55	19.5	0.182	0.228	0.228
166.2	75.2	3.30	16.5	0.200	0.246	0.244
160.4	60.3	3.20	15.1	0.212	0.256	0.256
153.3	43.1	2.52	10.9	0.231	0.272	0.270
149.0	26.2	4.31	17.7	0.243	0.278	0.279
145.2	30.4	4.90	19.6	0.250	0.289	0.288
140.3	19.2	2.68	10.2	0.263	0.298	0.300
134.8	30.2	5.51	20.4	0.270	0.314	0.313
130.6	35.3	5.15	18.4	0.280	0.326	0.325
124.2	20.6	3.10	10.4	0.298	0.341	0.342
118.7	20.4	3.07	9.7	0.316	0.362	0.358

The mean temperature and pressure of each observation are denoted by  $t_m$  and  $P_m$  respectively. They do not affect the calculation of  $c$  from  $C$  except in the small correction term  $nCP/T$ . The column headed  $c$  (obs.) represents the values of  $c$  obtained from those of  $C$  by the formula already given. The column headed  $c$  (calc.) represents the values of  $c$  corresponding to the temperature  $t_m$ , calculated by the formula  $c = c_1 (T_1/T_m)^{1/2}$ . The agreement of the observed and calculated values is seen to be within 1 per cent.,

which is good considering the nature of the observations. The values of the cooling-effect  $C$  are here expressed in degrees Centigrade drop of temperature for a drop of 1 lb. per sq. in. in the pressure. The corresponding values of  $c$  are in cubic foot per pound.

**32. Correction for External Heat-Loss.** It is most important in throttling experiments to reduce the external heat-loss to a minimum, because any loss of heat with superheated steam will lower the temperature and make the observed cooling-effect too large. It is also most important to avoid conduction of heat through the throttle from the high pressure steam. These objects were approximately attained by using a thin steel tube for the throttle, and by doubly jacketing the calorimeter with its own exhaust, as indicated in Fig. 5, in addition to external lagging. The residual error was further reduced in the differential method, by taking the difference of temperature between two similar calorimeters at slightly different pressures. The differential apparatus afforded a ready means of determining the residual correction. With this object the throttle tubes were made interchangeable, and tubes of different bores were employed, so that the temperatures could be observed under similar conditions with different currents of steam in the two calorimeters. By observing the difference of temperature when the current of steam was reduced in one of the calorimeters by fitting a smaller throttle, and the pressures were adjusted to equality, the external loss of heat could be readily deduced, from the observed values of the steam currents. A series of observations taken on this principle in the neighbourhood of  $300^{\circ}$  F., by the senior demonstrator Mr H. M. Jaquays in the Engineering Laboratory at McGill College during Nov. and Dec. 1897, showed that the required temperature correction was inversely proportional to the steam current (as would naturally be the case) and might amount to 5 or 10 per cent., according to the conditions of flow, with a single calorimeter, when the current of steam was at the rate of 1 pound per minute. A suitable correction was accordingly applied to the observations with the single calorimeter, which gave too large a value of the cooling-effect if the correction were omitted. With the differential apparatus the correction was found to be, if anything, in the opposite direction, since the calorimeter at the lower temperature had the smaller heat-loss; but the correction was so nearly eliminated by the differential method as to be of the same order as the accidental

errors of observation. Since the correction cannot be completely eliminated by lagging or jacketing, it would appear possible that the slightly larger values of the cooling-effect obtained by other observers, who have not employed the differential method, may be attributed to external heat-loss.

### 33. To Find the Total Heat of Steam by Throttling.

As already explained, the method adopted to find the initial value of the total heat of wet steam by the aid of the throttling calorimeter (when Regnault's values of the coefficients had been proved to be erroneous) was to construct a table of the values of the total heat of superheated steam at atmospheric pressure, deduced from those of the specific heat at atmospheric pressure obtained by the continuous electric method. The values of the specific heat obtained in this way in the first experiments were found to diminish from .50 to .49 with rise of temperature from 100° to 160° C., and gave results for the total heat practically identical with those in the following table.

Table II. Values of Total Heat of Superheated Steam at Atmospheric Pressure.

Temperature		Single degrees Centigrade												
C.	F.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°	11°	12°
200°	392°	688.53	89.01	89.50	89.99	90.48	90.96	91.45	91.94	92.42	92.91	93.39	93.87	94.35
190°	374°	683.66	84.14	84.63	85.12	85.60	86.09	86.58	87.07	87.55	88.04	88.52	89.00	89.48
180°	356°	678.79	79.27	79.76	80.25	80.74	81.22	81.71	82.20	82.68	83.17	83.65	84.13	84.61
170°	338°	673.91	74.40	74.88	75.37	75.86	76.35	76.83	77.32	77.81	78.30	78.78	79.26	79.74
160°	320°	669.01	69.50	69.99	70.48	70.97	71.46	71.95	72.44	72.93	73.42	73.90	74.38	74.86
150°	302°	664.10	64.60	65.09	65.58	66.07	66.56	67.05	67.54	68.03	68.52	69.00	69.48	69.96
140°	284°	659.18	59.68	60.17	60.66	61.15	61.65	62.14	62.63	63.12	63.61	64.09	64.57	65.05
130°	266°	654.24	54.73	55.23	55.72	56.21	56.71	57.20	57.70	58.19	58.68	59.16	59.64	60.12
120°	248°	649.29	49.78	50.28	50.77	51.27	51.76	52.26	52.75	53.25	53.74	54.22	54.70	55.18
110°	230°	644.31	44.81	45.31	45.80	46.30	46.80	47.30	47.80	48.29	48.79	49.27	49.75	50.23
100°	212°	639.30	39.81	40.31	40.81	41.31	41.81	42.31	42.81	43.31	43.81	44.30	44.79	45.27
		0°	1.8°	3.6°	5.4°	7.2°	9.0°	10.8°	12.6°	14.4°	16.2°	18.0°	19.8°	21.6°
Degrees and decimals Fahrenheit														

By observing the temperature  $t''$  of the steam when throttled to atmospheric pressure, the total heat of the throttled steam, and therefore of the initial steam, is immediately given by reference to the table. The observed temperature  $t''$  requires careful correction for thermometric errors, especially stem-exposure, if mercury thermometers are employed. It should also be corrected for external heat-loss, which is most easily done by using a differential

calorimèter with a double throttle tube on one branch, so that the current through one side is double that through the other. The difference of temperature when *both* are at atmospheric pressure, gives the correction to be added to the higher reading. The method is perfect so far as the sample taken is concerned, but it is important to make sure that the sample taken is a fair sample of the main steam supply to the engine under test. The method has the advantage of applying equally to wet steam or superheated steam, provided that the total heat is not outside the limits of the table.

**34. Curves of Constant  $H$  on the  $PT$  Diagram.** The general results of the application of the Joule-Thomson method to steam are best represented graphically by drawing the curves of constant total heat on the pressure-temperature diagram as shown in Fig. 9, in which the pressure in lbs. per sq. in. abs. is taken as abscissa, and the temperature in degrees Centigrade as the ordinate. The full lines shown in the figure, extending from the line of zero pressure to the saturation curve, are lines of constant total heat calculated by the author's formulae, based on the experiments with the differential throttling calorimeter, and on the measurements of the specific heat of steam at atmospheric pressure. The dotted lines marked Pa, G1, and Gs11, represent the highest series of observations made by Peake, Grindley and Griessmann, respectively, who traced the lines of constant  $H$  by keeping the initial state as constant as possible while the steam was throttled to various lower pressures in succession. These are seen to correspond as closely as could be expected with each other and with the theoretical curves.

The dotted lines TT and ZZ in the figure, are calculated from the characteristic equations of Tumlriz and Zeuner, respectively, which were most commonly employed in 1900, and for some years later, in expressing the properties of steam. These curves are seen to be of a different type, and do not show a satisfactory correspondence with experiment.

According to Zeuner (*Zeit. Ver. Deut. Ing.* xi, p. 41, 1867) the properties of steam are represented by the characteristic equation

$$PV = 50.933T - 192.5P^{\frac{1}{2}}, \dots\dots\dots(1)$$

where  $P$  is the pressure in kilograms per square metre, and  $V$  the specific volume in cubic metres per kilogram, so that  $PV$  is in kilogrammetres. This equation requires that the value of the

product  $SC$ , deduced from III (8), should be  $192.54P^{-\frac{1}{2}}$ , and should be independent of the temperature. It follows by III (12) that  $S$  must be independent of the pressure, but may be any function of the temperature. Zeuner assumed  $S$  constant and equal to 0.4805, with  $A = 1/424$ , so that  $C = 0.945P^{-\frac{1}{2}}$ , which is always the same at the same pressure, and becomes infinite at  $P = 0$ . The numerical value of  $C$  at a pressure of 1 kg./sq. cm. (10,000 kg./sq. m.) is 9.45° C. per atmosphere (1 kg./sq. cm.) in (K.M.C.) units. Similarly at  $P = 16$  kg./sq. cm. we have  $C = 9.45/8$  (K.M.C.).

The equation of a line of constant total heat is obtained by integrating  $CdP = dT$  at constant  $H$ . If  $C = 9.45P^{-\frac{1}{2}}$ , as in Zeuner's equation, we thus obtain for a line of constant  $H$  starting from  $T_0$  at  $P = 0$

$$T - T_0 = 37.8P^{\frac{1}{2}} \text{ (K.M.C.)} = 19.46P^{\frac{1}{2}} \text{ (F.P.C.)}.$$

The dotted line  $ZZZ$  in Fig. 9 represents such a line starting from  $T_0 = 395^\circ$ , or  $t_0 = 122^\circ$  C. According to this equation the lines of constant  $H$  are all exactly similar to  $ZZZ$ , e.g. the line starting from  $100^\circ$  C. would be obtained by simply shifting the curve down through  $22^\circ$  C. The values of  $C$  are of the right order of magnitude at average pressures and temperatures such as  $P = 50$  lbs. and  $t = 150^\circ$  C., but the curves are evidently of the wrong type,

The characteristic equation of Tumlirz (*Sitz. Akad. Wien*, II a, p. 1058, 1899), may be put in the numerical forms

$$V = 0.00467T/P - 0.008402 \text{ (K.M.C.)} = 1.07T/P - 0.1846 \text{ (F.P.C.)}.$$

.....(2)

According to this equation, the defect of  $V$  from the ideal value is constant and equal to 0.0084 cb. m./kg., which is about three times too small at  $100^\circ$  C. The product  $SC$  is also constant and equal to 0.0084 kilocalories per unit pressure-drop of 1 kg./sq. m., or to 0.197 per atmosphere (K.M.C.). The specific heat is independent of the pressure, but may be any function of the temperature. Tumlirz assumed  $S$  constant and equal to 0.48, which gives  $C = 0.197/0.48 = 0.412^\circ$  C. for a pressure-drop of 1 kg./sq. cm. at any point of the diagram. According to the equation of Tumlirz, the lines of constant  $H$  are parallel straight lines with a slope  $C = 0.412^\circ$  (K.M.C.), or  $0.029^\circ$  (F.P.C.), as indicated in the figure by the dotted lines marked  $TT$ , which have evidently much too small a slope to agree with experiment.

According to the author's theory, the cooling-effect is a function

of both temperature and pressure, but the curves of constant  $H$  are readily drawn by putting  $H$  constant in the general expression for  $H$  given by equation (24) of Chapter III. Putting  $H = S_0 T_0 + B$ , we thus obtain

$$S_0(t - t_0) = SCP, \dots\dots\dots(8)$$

where  $t_0$  is the temperature at which the line considered cuts the vertical axis  $P = 0$ , and is given by  $(H - B)/S_0 - 273$ , in terms of the value of  $H$  for the line considered.

It is very easy to draw the lines of constant total heat with the aid of this equation by taking the values of  $SC$ , given for each  $10^\circ \text{C}$ . in Table I, and also in Table IV of the Steam Tables, Appendix III. If it is desired to draw the line passing through any arbitrary point  $P''T'$ , the corresponding value of  $S'C''$  must be found by interpolation, and the equation becomes for dry steam,

$$S_0(t - t') = SCP - S'C''P', \dots\dots\dots(4)$$

where  $t'$  is the Centigrade temperature corresponding to  $T'$  abs. It is easy to calculate  $P$  by the aid of this equation for any given value of  $t$ .

If on the other hand, the initial temperature and pressure  $t'$ ,  $P'$  are given and it is required to find the final temperature  $t''$  when the steam is throttled to a given pressure  $P''$ , it is necessary to proceed by interpolation, as in the following example:

- *Example.* If the initial state is given as 173 lbs. at  $187.2^\circ \text{C}$ ., find the temperature after throttling to atmospheric pressure.

At  $P' = 173 \text{ lbs.}$ ;  $t' = 187.2^\circ \text{C}$ .  $S'C''$  (interpolated) = 0.0915,  $S'C''P' = 15.82$ .

At  $P'' = 14.7 \text{ lbs.}$ ;  $t'' = 150^\circ$  (trial);  $S''C'' = 0.12187$  (table);  $S''C''P'' = 1.80$ , whence  $t' - t'' = (15.82 - 1.80)/0.4772 = 29.4^\circ$ .  $t'' = 157.8^\circ \text{C}$ .

If  $t'' = 160^\circ$  (trial),  $S''C'' = 0.11256$  (table);  $S''C''P'' = 1.64$ , whence  $t'' = 157.5^\circ$ .

The required answer is evidently  $157.6^\circ \text{C}$ . The trial value assumed for  $t''$  makes very little difference if the pressure  $P''$  is low. The value of  $t''$  first obtained will be a good approximation, and will show how much the trial value was too high or too low. The approximation is so rapid, that a second trial is seldom required.

If the steam is throttled to atmospheric pressure, a convenient method is to find the initial value of the total heat in the Steam Tables, from Table III ( $H$ ), or Table IV, and then find the tem-



perature giving the same value of  $H$  at atmospheric pressure from Table II of this chapter for each  $1^\circ \text{C}$ .

The value of the cooling-effect at the mean temperature and pressure of any range is found approximately by dividing the value of  $SC$  at the mean point by the value of  $S$  near the same point taken from Table IV of the Steam Tables. In an experiment in which  $P'$ ,  $t'$ ,  $P''$ ,  $t''$  are the observed quantities, the observed mean cooling-effect,  $C = (t' - t'')/(P' - P'')$ , may most easily be verified in this way.

**35. Results of other Observers.** Curves of constant total heat on the  $PT$  diagram were first exhibited in the manner shown

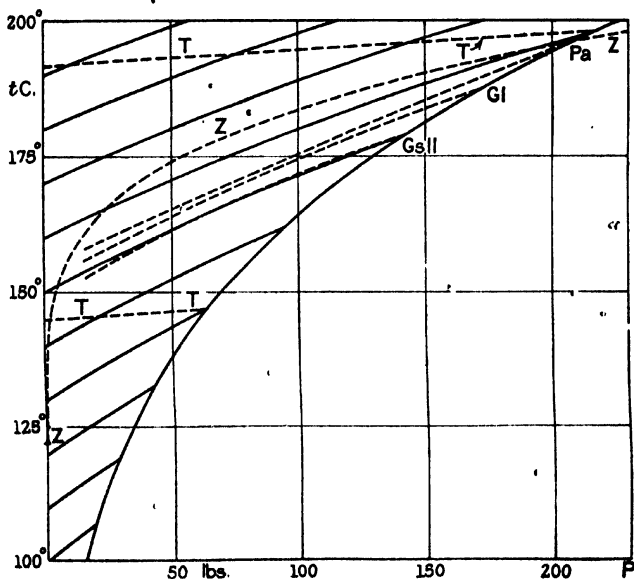


Fig. 9. Lines of constant  $H$ .  $PT$  diagram.

in Fig. 9, by Grindley (*Phil. Trans. A*, 194, p. 1) to represent the results of his experiments by the throttling method. Each curve was obtained by keeping the initial pressure of the saturated steam as nearly constant as possible, and observing the temperatures after throttling to various lower pressures. Values of the specific heat were deduced by assuming Regnault's formula for the total heat of saturated steam. Taking any pair of curves, the difference

of total heat  $H' - H''$  is on this assumption equal to 0.305 multiplied by the difference of initial temperatures ( $t_s' - t_s''$ ) of the saturated steam. The specific heat at any constant pressure is the difference  $H' - H''$  divided by the difference of temperature ( $t' - t''$ ) between the two curves at the required pressure.

$$S = 0.305 (t_s' - t_s'') / (t' - t'') \dots \dots \dots (5)$$

The values of  $S$  calculated by Grindley in this way showed a rapid increase with temperature, but appeared to be nearly independent of the pressure. The product  $SC$  appeared to be nearly constant at all temperatures and pressures within the experimental range. This led to a characteristic equation of the same form as that of Tumlirz, but with quite a different value of the constant, namely,

$$aPV = RT - 0.2817P \text{ (F.P.F.)} = RT - 0.1565P \text{ (F.P.C.)}$$

$$\text{or } V = RT/aP - 1.522 \text{ (F.P.F. or C.)} = RT/aP - 0.0950 \text{ (K.M.C.),}$$

where the coefficient of  $P$  is the constant value of  $SC$  on either system. The defect of volume given by this equation is about six times too large at  $150^\circ \text{C}$ .

It is evident that an equation of this type, with  $S$  variable, can be fitted fairly well to the throttling curves, but the values of  $S$  required do not agree with direct experiments on the specific heat. It is easy to calculate the values of  $S$  and  $C$  on this hypothesis by the equation (see § 23)

$$(dH/dT)_s = 0.305 = S - SC (dp/dt), \dots \dots \dots (6)$$

since both  $S$  and  $C$  must be independent of the pressure. We thus obtain

Table III. Values of  $S$  and  $C$  by Grindley's Equation.

Temp. Cent.	100°	120°	140°	160°	180°	200°	220°	240°
$dp/dt$ , lbs./° C.	0.525	0.914	1.488	2.284	3.335	4.675	6.290	8.175
$S$ , cal./° C.	0.387	0.448	0.538	0.662	0.827	1.037	1.289	1.584
$C$ , ° C./lb.	0.404	0.349	0.291	0.236	0.189	0.151	0.121	0.099

The values of  $C$  are in fairly good agreement with experiment, but  $S$  cannot be so low as 0.387 at  $100^\circ \text{C}$ ., or so high as 1.087 at  $200^\circ \text{C}$ .; and there is very strong evidence that  $S$  is not independent of the pressure. Grindley did not actually make this calculation, but it is fairly deducible from his equation and data (see *R. S.* 1900, 67, p. 279).

Grindley endeavoured to eliminate external loss of heat by surrounding his throttling chamber with a massive cast-iron jacket containing saturated steam, the pressure of which was adjusted by the aid of an auxiliary thermo-couple to give the same temperature as that of the throttled steam, a method suggested by Prof. Osborne Reynolds. The objection to this method was that it took a long time (2 or 8 hours) to reach a steady state, which is a serious matter when observations have to be taken successively at different pressures and temperatures. Grindley's longest curve is shown in the preceding figure, marked G1. It has a slightly steeper slope than the author's, which may possibly be explained by the fact that his initial steam was always slightly wet, or that his method of eliminating the heat-loss was less effective than the differential method. The average values of the cooling-effect for each of his six curves of constant  $H$ , are most readily compared with the author's by calculating the value of  $t_0$  at zero pressure for each curve by equation (8) as in the following table.

Table IV. Temperature  $t_0$  at zero pressure from Grindley's Throttling Curves.

	Number of Curve					
	(1)	(2)	(3)	(4)	(5)	(6)
$t_0$ observed (Grindley)	151.7	142.2	127.8	122.8	113.9	105.0
$t_0$ calc. (Callendar)	154.2	143.8	128.9	123.0	114.3	105.7
" " (Zeuner)	114.6	112.4	86.5	80.5	73.0	65.1
" " (Tumlirz)	180.0	163.8	142.5	134.7	123.6	112.6

The results are evidently incompatible with the equations of Zeuner or Tumlirz, but the general agreement with the author's equation is good, apart from the small systematic difference already explained.

Grindley employed an orifice in a thick glass plate as a throttle, which gave some trouble in fitting, and frequently cracked, but probably served fairly well to prevent excessive conduction of heat from the high pressure side to the throttled steam.

**36. Results of Griessmann and of Peake.** Griessmann (*Ver. Deut. Ing.* 47, p. 1852, 1908), who repeated Grindley's experiments at Dresden under Prof. Mollier, employed a porous plug of the Joule-Thomson type, consisting of layers of canvas, embedded in a thick block of wood for heat insulation. His highest curve,

marked Gs11, is shown in Fig. 9 dotted. It happens to fall very nearly on one of the author's curves from  $150^{\circ}$  to  $179^{\circ}$ , but has a slightly greater curvature. All Griessmann's lines of constant  $H$  are more highly curved than those of the other observers, indicating a more rapid increase of  $C$  with fall of temperature and pressure.

A large block of porous non-conductor, like wood, has a considerable thermal capacity and a very awkward kind of memory. It is also liable to become damp when exposed to saturated steam, and the evaporation of the moisture involves great loss of heat when the pressure is reduced. This affords a possible explanation of the many low points shown on his curves, and the systematic tendency to excessively high values of  $C$  at low pressures.

Griessmann reduced his observations on much the same lines as Grindley. Taking Regnault's value for  $(dH/dT)_s$ , namely 0.805, he found a similar variation of  $S$  with temperature. He also found that the product  $SC$  was nearly independent of the temperature at constant pressure, indicating that  $S$  was independent of the pressure, as in Zeuner's equation. He thus obtained a form of characteristic equation similar to Grindley's, but with this difference, that  $SC$  varied slightly with the pressure. The values found for  $SC$  ranged from about 2.20 (K.M.C.) at 1 kg./sq. cm. to 1.80 at 5 kg. The values of the volume deduced from this equation showed fair agreement with Zeuner's. Griessmann's main conclusion was that Zeuner's equation was accurate over the experimental range; but he does not appear to have noticed that Zeuner's equation requires a very different variation of  $SC$ , namely from 4.50 (K.M.C.) at 1 kg./sq. cm. to 0.564 at 16 kg.

Peake (*Proc. R. S.* 76, p. 185, 1905) employed a perforated mica disc as throttle, and jacketed the calorimeter with its own exhaust. His curves of constant  $H$ , one of which, marked Pa, is shown in Fig. 9, were all very nearly straight lines. This would indicate that  $C$  remains nearly constant at constant  $H$ , or that the increase of  $C$  with fall of temperature is nearly compensated by a diminution with fall of pressure; whereas Grindley found that  $C$  varied as  $T^{-4}$  nearly, but was practically independent of the pressure. Otherwise his curves were similar to Grindley's, but showed a somewhat steeper slope, due probably to less perfect elimination of the heat-loss. He also made some incomplete experiments on the specific heat at atmospheric pressure by an electric method, which gave 0.48 as the mean value between  $300^{\circ}$  and  $200^{\circ}$  C., and showed no variation with temperature such as Grindley had found.

### 37. Variation of $C$ with Temperature and Pressure.

Experiments such as those described, with a single throttling calorimeter, though affording the simplest method of observing the lines of constant  $H$ , provided that the initial state can be kept constant, are not well suited, as already explained, for determining the variation of  $C$  with temperature or pressure. The drawing of smooth curves through the observed points is to a great extent a matter of taste, and the drawing of tangents to such curves affords considerable scope for imagination. Empirical formulae are equally misleading because the type of formula selected is the main factor in determining the result found. The least objectionable method is to take the actual observations in pairs along any one curve, and to find the value of  $C$  for each interval by taking the ratio of the temperature and pressure differences. Values found in this way from neighbouring pairs of points are apt to be very discordant, as would naturally be expected, but the method has generally been adopted by the experimentalists themselves, and by others in reducing their results. In addition to affording an instructive illustration of the theory, the method deserves discussion because it appears in some cases to lead to results at variance with those of the differential method.

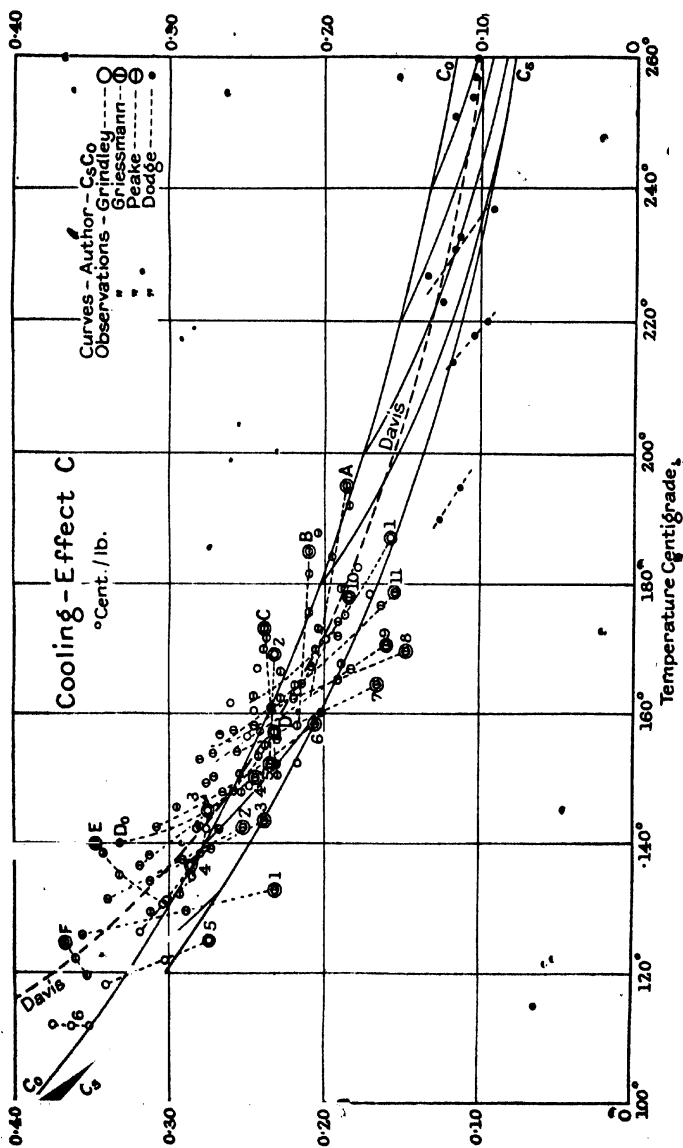
This method of reduction has been very carefully and impartially applied to all the results quoted by Prof. H. N. Davis of Harvard (*Proc. Amer. Acad. Sci.*, 45, p. 243, 1910), whose conclusions have in many cases been accepted as more directly representing the results of experiment than the author's theoretical method. In applying this method Prof. Davis has found it necessary to reject several of the observations, which are obviously affected by variations in the quality of the initial steam, and would give absurdly high or low values of  $C$ . This eliminates many of the worst outliers in the resulting  $CT$  diagram, but cannot mitigate any systematic error in the smoothing of the curves, especially near the ends. He attributes the residual discrepancies chiefly to the employment of mercury thermometers for all the temperature readings, and spring-gauges for the pressure readings, in place of electrical thermometers or mercury gauges, which are much better suited for reading small differences. The discrepancies of individual observations are further reduced by taking means of neighbouring groups. There is room for taste in the matter of rejection and grouping of observations, but it appears from reference to the original observations that the points selected by Davis may be accepted for purposes

of argument as fairly representing the results of the experiments. The points have accordingly been verified and replotted in Fig. 10 on a different scale (F.P.C.) to show the cooling-effect in degrees C. for a pressure-drop of 1 lb./sq. in. The points belonging to different observers have been distinguished by the same marks as those employed by Davis, namely, plain circles for Grindley's observations, circles with a vertical cross-bar for Griessmann's, and with a horizontal cross-bar for Peake's. Some additions have been made to the diagram in the hope of rendering it more intelligible.

Davis states that he examined the results with great care for evidence of any systematic variation of  $C$  with pressure at constant temperature, but without success. He accordingly represented the cooling-effect as a function of the temperature only by a simple curve, shown in his paper on a different scale in a separate figure. This curve is reproduced as nearly as possible by the broken line marked "Davis" in Fig. 10. It appears to represent the observations fairly from high temperatures down to  $150^{\circ}\text{C.}$ , but gives too much weight to Peake's observations at low temperatures.

The results of the author's differential method are represented by the two full curves marked  $C_0$  and  $C_s$ . The upper curve represents the limiting values of  $C$  at zero pressure, the lower curve the values of  $C$  at saturation pressure. The somewhat steeper lines joining the two curves indicate the variation of  $C$  at constant total heat, which is more rapid, owing to the combined effects of drop of temperature and pressure, which both tend to increase  $C$ .

In order to be able to estimate the value of the evidence afforded by the different series of observations, it is necessary to group them, as originally taken, along lines of constant total heat. The dotted lines indicate as closely as possible the connection of the points obtained from each of the original curves of constant  $H$ . These lines are produced backwards to the saturation temperature in each case. The points so obtained are surrounded with larger circles, and are marked with the letter or number given by each observer in his original paper. The double circles with horizontal cross-bars marked A, B, C, D, E, F, indicate the starting points of Peake's lines of constant  $H$ ; those with vertical cross-bars numbered 11 to 1, indicate Griessmann's; the plain double circles, numbered 1, 2, 3, 4, 5, indicate Grindley's. Curve No. 6 Grindley, cannot be extrapolated to saturation, because the line is so short that only one satisfactory point can be obtained from each of the three series of observations represented on the curve.

Fig. 10. Results of other observers for  $C$ .

It is immediately obvious that nearly all of Peake's values at the higher pressures are much too high, especially for line *E*, the two highest points on which were rejected by Davis on this account, but have been replaced in Fig. 10. The Davis curve appears, however, to give great weight to the highest observation on curve *F* as compared with Grindley's points on 5 and 6, which are quite satisfactory. It is not theoretically inconceivable that *C* should increase with increase of pressure, as shown by Peake's curves, but it is against the other experimental evidence. Moreover Peake's curve *D* is inconsistent with his other curves in this respect. The point on this curve at the low pressure end, marked  $D_0$ , approaches very closely to the high pressure end of *E*.

All of Griessmann's curves, on the other hand, as one would expect from their excessive curvature, show a very rapid increase of *C* with fall of *T* and *P* at constant *H*, and give exceptionally low values of *t* at low pressures, as might be predicted from the obvious experimental errors of the points rejected by Davis and by Griessmann himself. It is possible however that Griessmann's points near saturation may be fairly reliable, because the error due to evaporation from the wood block is most to be feared at low pressures.

All of Grindley's curves (except No. 2, where the points are so discordant that no satisfactory indication is given) show a reasonable slope. One may fairly set Griessmann's observations against Peake's, and conclude that the intermediate slope of the lines of constant total heat, indicated by the author's differential method, is not in reality inconsistent with the results of these experiments. Without some guidance from theory it is hopeless to attempt to draw a mean curve through a target-diagram of this kind, especially near the low pressure end of the range, where the observations are few and the curves short. Grindley's results are the most reliable in this region since he was the only one of the three to use a vacuum condenser.

The variation with pressure deduced from the author's formula is corroborated at high temperatures by the work of A. R. Dodge (*Am. Mech. Eng.* 80, p. 728), four of whose lines of constant *H* are indicated in the figure between 190° and 260° C., the observations being marked by black dots. The pressure range extended from 214 to 37 lbs., and the lower dots on each line represent the higher pressures. The points between 250° and 260° C. happen to fall almost exactly in their appropriate places on one of the author's



lines of constant  $H$ , but those at lower temperatures are evidently too low, though they all show the same kind of variation of  $C$  with pressure as the author's formula.

Further experiments on the cooling-effect are undoubtedly desirable, but the evidence so far available tends to support the previous conclusions, and is far from justifying the adoption of any more complicated formula.

### 38. Later Experiments by the Differential Method.

The differential throttling calorimeter was redesigned for higher pressures and temperatures in conjunction with Prof. Dalby in 1906, and was set up in the thermodynamic laboratory of the City and Guilds' Institution (now part of the Imperial College of Science) at South Kensington. The late Prof. Ashcroft assisted the author in taking a series of observations on the cooling-effect, at high temperatures. Differential platinum thermometers were employed for the temperature differences, and a differential mercury gauge for the pressure differences. The observations extended to an upper limit of  $876^{\circ}\text{C.}$ , and agreed so closely with the variation of the cooling-effect predicted by the equations previously given, that it was not considered worth while to publish them in detail, as it was hoped to obtain a more complete series at higher pressures as soon as a special boiler and regulator could be installed. Unfortunately the rapid increase in the number of students under Prof. Dalby, which necessitated a continual rearrangement of laboratories and the erection of new buildings, and greatly curtailed the funds and assistance available for research, made it impossible to proceed further with the work at the time. It was concluded that the variation of  $C$  was represented with sufficient approximation for all practical purposes at moderate pressures by the formulae already published, and that no modification should be made in the equations unless decisively necessitated by the proposed experiments at higher pressures.

From a theoretical standpoint, the most important question remaining to be settled is the variation of  $C$  with pressure at constant temperature, with regard to which the results of other observers are so contradictory. It is a difficult point to investigate, even by the differential method. Unfortunately the original experiments at McGill College were interrupted at a crucial stage before it had been possible to attack this question effectively. The experiments had been arranged to cover the temperature

range from  $120^{\circ}$  to  $180^{\circ}$  C., but, in the absence of a superheater, the observations threw little light on the variation with pressure. They might in fact have been represented fairly well by assuming that  $C$  was a function of the temperature only. The pressure available in the later experiments at the City and Guilds' Institution being limited to 50 lbs., it was decided to restrict the investigation to the variation of  $C$  with temperature, since there was no satisfactory prospect of settling the variation with pressure. Very few observations were obtained at temperatures below  $180^{\circ}$  C. These seemed to indicate that the pressure variation was, if anything, less than that given by the form of characteristic equation previously assumed, but since the conditions of experiment were somewhat different, no great stress could be laid on the small differences found. It is very easy however to examine the question theoretically and to show how little difference it makes to the results for practical purposes over the experimental range.

**39. Alternative Theory,  $C = F(T)$ .** In the preceding theory we have assumed that the coaggregation volume  $c$  and the product  $SC$  are functions of the temperature only, because this leads to the simplest possible form of characteristic equation, and represents all the experimental results satisfactorily for practical purposes over the necessarily restricted range of the actual observations. It is of considerable interest from a theoretical standpoint to investigate the effect of some alternative hypothesis. The obvious alternative to select is that the cooling-effect  $C$  is a function of the temperature only. The theoretical relations thus obtained are sufficiently simple to be intelligible, and are greatly to be preferred to any purely arbitrary or empirical equations.

If  $C$  is a function of the temperature only, the equation of a line of constant total heat is immediately obtained by integrating  $dP = dT/C$ . We have also a very useful result which follows from the general relations (Appendix I (87)),

$$(dSC/dP)_H = C (dSC/dT)_H = S (dC/dP)_T, \dots\dots\dots(7)$$

namely that  $SC$  is constant along a line of constant  $H$ , since  $(dC/dP)_T = 0$ , if  $C$  is a function of the temperature only. It is therefore very easy to draw the lines of constant  $H$ , and to find the value of  $S$  at any temperature and pressure, if the value  $S_0$  at zero pressure is known. We have evidently  $S = S_0 C_0/C$ , where  $C_0$  is the value of  $C$  at  $T_0$  and zero pressure on the given line of constant  $H$ . It is easy to allow for the variation of  $S_0$  with tem-

perature if desired, but for the present purpose we may take it as constant, in which case we have the simple relation

$$H = S_0 T_0 + B,$$

at zero pressure.

By way of illustrating the method, we may take the simple case

$$C = K/T^n = C_1 (873/T)^n, \dots\dots\dots(8)$$

where  $C_1$  is the value of  $C$  at  $100^\circ \text{C.}$  or  $373^\circ \text{abs.}$  The equation of a line of constant  $H$  is evidently

$$(n+1)KP = T^{n+1} - T_0^{n+1}, \dots\dots\dots(9)$$

where  $T_0$  is the value of  $T$  when  $P = 0$ .

The general expression for  $H$  is found by substituting

$$T_0 = (H - B)/S_0.$$

After a few simple reductions we obtain

$$H - B = S_0 T (1 - (n+1) CP/T)^{1/(n+1)}, \dots\dots\dots(10)$$

The general expressions for  $S$  and  $SC$  are readily obtained by differentiation, and satisfy the required condition  $SC = S_0 C_0$ .

The characteristic equation for  $V$  is obtained by integrating that for  $SC$ ,

$$a(T(dV/dT)_P - V) = SC = S_0 C (1 - (n+1) CP/T)^{-n/(n+1)}, \dots\dots\dots(11)$$

which becomes an exact differential on dividing by  $T^2$ , and gives, if  $S_0 = (n+1)R$ ,

$$aPV/RT = (1 - (n+1) CP/T)^{1/(n+1)}, \dots\dots\dots(12)$$

which evidently satisfies condition (14) of the last chapter for the adiabatic equation  $P/T^{n+1} = K$ .

All the equations show a very close correspondence with those previously given, except that the small quantity  $b$  has been omitted\* in order to make the work easier to follow. The numerical results obtained from the two sets of equations are also in practical agreement over the experimental range, but begin to diverge beyond  $200^\circ \text{C.}$ , where experimental data, except for the saturation pressure, are practically non-existent.

The form of solution thus obtained differs materially from that

\* The small quantity  $b$  is most readily included in equation (12) by putting  $H - B = a(n+1)P(V-b) + abP$  in (10), which reduces to (12) with  $b$  included.

originally given by Joule and Thomson and repeated in all the mathematical textbooks at the present day. Taking the special case which Joule and Thomson adopted, namely  $n = 2$ , or  $C = K/T^2$ , and accepting the condition that the specific heat  $S_0$  at zero pressure is constant, we find that the solution must be of the form

$$aPV/RT = (1 - 3KP/T^3)^{\frac{1}{3}}, \dots\dots\dots(13)$$

provided that  $S_0$  is equal to  $3R$ , but takes the form

$$aPV/RT = (S_0/3R) (1 - 3KP/T^3)^{\frac{1}{3}} + 1 - S_0/3R, \dots(14)$$

if  $S_0$  differs from  $3R$ , the constant of integration in either case being determined by the condition that  $aPV = RT$  when  $T$  is infinite. In the limit, when  $P$  is small, equation (14) evidently reduces to the form

$$aPV/RT = 1 - KS_0P/3RT^3, \dots\dots\dots(15)$$

which agrees with that given by Joule and Thomson; but the equation in this form is inconsistent with their original assumption that  $C$  was independent of the pressure. The reason of the discrepancy is simply that Joule and Thomson, in integrating the equation, in reality assumed  $SC = KS_0/T^2$ , or  $SC$  a function of the temperature only, in place of assuming  $C = K/T^2$ . The solution which they obtained is consequently inconsistent with  $C = K/T^2$ , and with  $S = \text{constant}$ , and requires some variation of  $S$  with pressure and temperature even if  $S_0$  is constant. The inconsistency of the solution thus obtained was relatively unimportant for their purpose as compared with experimental errors, but is the *essential point* in considering the effect of the alternative assumption that  $C$ , in place of  $SC$ , is a function of the temperature only. Since the form of characteristic equation obtained on this assumption, though theoretically interesting, is inconvenient for practical purposes, and makes very little difference in the results over the experimental range, there appears to be no sufficient reason for adopting it in preference to the simple form previously employed.

**40. Second Alternative,  $C = F(H)$ .** It is of interest to examine in the same way another possible assumption, suggested by the straightness of Peake's lines of constant  $H$ , namely that  $C$  is a function of  $H$  only. The equation of a line of constant  $H$  is the straight line,  $CP = T - T_0$ , and the general expression for  $H$  deduced in the same way as before becomes

$$H = S_0T - S_0CP + B, \dots\dots\dots(16)$$

which is the same as equation (24) of the last chapter, except that

$SCP$  is replaced by  $S_0CP$ , and that  $C$  is a function of  $H$  only, in place of  $SC$  being a function of  $T$  only.

To obtain a solution comparable with those previously given, we assume

$$C = K/(H - B)^n = C_1 (S_0 T_1 / (H - B))^n, \dots\dots\dots (17)$$

where  $C_1$  is the value of  $C$  at  $T_1$  and zero pressure.

A consistent form of characteristic equation is most easily obtained by assuming that the adiabatic is of the form

$$P/T^{n+1} = \text{constant},$$

and substituting  $a(n+1)PV$  for  $H - B$  in the equation for  $H$ , which gives immediately

$$aPV = RT - RC_1P (RT_1/aPV)^n. \dots\dots\dots (18)$$

This equation is less convenient in form than either of those previously given, because  $V$  is not obtainable explicitly as a function of  $P$  and  $T$ . If  $b$  is omitted, all three equations agree exactly in the limit at low pressures provided that equivalent values of the constant  $c_1 = RC_1/a$  are employed. But better agreement is obtained over the experimental range by selecting slightly different values of the constant  $C_1$  together with appropriate values of  $b$ . The agreement is of much the same order as that between the observations of Grindley, Griessmann and Peake on the cooling-effect. Without employing the differential throttling method, it would in fact be difficult to decide between the three equations by experiments on the cooling-effect alone between  $120^\circ \text{C.}$  and  $180^\circ \text{C.}$ , but the form first given is much the simplest in application, and gives the best agreement with other properties over the experimental range. Thus if the values of the cooling-effect in the three equations are chosen to agree with experiment at  $180^\circ \text{C.}$  and 50 lbs., the assumption  $C = F(T)$ , represented by equation (10) would make the total heat of saturated steam a maximum at  $232^\circ \text{C.}$ , (where  $Cdp/dt = 1$ ) which is improbable; but equation (16) with  $C = F(H)$ , would make  $H$ , a maximum at a temperature close to  $200^\circ \text{C.}$ , which is irreconcilable with experiment.

#### 41. Values of $H$ deduced from $C$ by Extrapolation.

Since the main object of experiments on the cooling-effect is to deduce the variation of  $H$ , it is most instructive, in comparing possible types of formula for  $C$ , giving reasonable agreement over the experimental range, to consider the effect of each on the values

of  $H$  deduced by extrapolation. If the values of the saturation pressure  $p$  are given, it is easy to deduce the values of  $H$ , corresponding to any simple assumption with regard to  $S_0$  and  $C$  beyond the experimental limits. Although the values of  $S_0$  and  $p$  are somewhat uncertain at high temperatures in the neighbourhood of the critical point, the comparison of different formulae for  $C$  is little affected thereby, provided that the same values of  $S_0$  and  $p$  are taken in each case.

In order to simplify the comparison as much as possible, we may take  $S_0$  constant and equal to 0.4772, since the variation is probably small. The formula selected for  $p$  is

$$\log_{10} p = 2.3526 + 4.264 (t - 200)/T, \quad (\text{F.P.C. from } 200^\circ \text{ to } 374^\circ \text{ C.}),$$

$$\dots\dots(19)$$

which gives the simple expression  $(T/p) (dp/dT) = 4645/T$  for the ratio of  $L$  to  $ap(V - v)$ . This is the simplest possible type of formula for  $p$ , and has been found to give results within the limits of experimental error at high pressures for most liquids, although it is certainly inaccurate at low pressures. The constants in the formula have been chosen to give the same values as the author's formula for both  $p$  and  $dp/dT$  at  $200^\circ \text{ C.}$ , so that the two curves join continuously at this point. It probably gives values which are too high between  $250^\circ$  and  $300^\circ \text{ C.}$ , but the uncertainty at any point between  $200^\circ$  and  $374^\circ \text{ C.}$  is less than the discrepancies between the results of different experimentalists.

Taking first the assumption  $C = F(H)$ , we observe that in order to represent the variation of slope of successive lines of constant  $H$  at low pressures between  $120^\circ$  and  $180^\circ \text{ C.}$ , it is necessary that  $C$  should vary approximately as  $1/(H - B)^{1.8}$ . Taking  $C = 0.350^\circ \text{ C./lb.}$  at  $100^\circ \text{ C.}$  and 1 atmosphere, the lines of constant  $H$  become tangential to the saturation curve (giving a maximum value of  $H$ , and a minimum value of  $C$ , when  $C_s (dp/dt) = 1$ ) at a temperature a little above  $200^\circ \text{ C.}$  Beyond this point the value of  $C$  must increase with rise of temperature, and the value of  $H$  must diminish very rapidly. Thus the line of constant  $H$  passing through the point  $t = 120^\circ \text{ C.}, P = 20 \text{ lbs.}$ , with  $H - B = 184.5$ ,  $C = 0.298$ , cuts the saturation curve a little above  $120^\circ \text{ C.}$ , and cuts it again at  $p = 880$ ,  $t = 227^\circ$ . But the line through  $t_s = 100^\circ$ ,  $C = 0.850$ , cuts it again at a lower point, namely,  $t = 225^\circ$ ,  $p = 867 \text{ lbs.}$ , and the line through  $t = 0^\circ \text{ C.}, H = 394.8$ ,  $C = 0.955$ , cuts it again at  $195^\circ \text{ C.}$  None of the lines of constant  $H$  can cut the saturation

curve at all at any temperature higher than  $227^{\circ}\text{C.}$ , or can pass anywhere near the critical point. In order to pass through the critical point at  $T = 647^{\circ}$ ,  $p = 8160$ ,  $H = h = 464$ , the line through the absolute zero must have a slope

$$C = 647/8160 = 0.0205,$$

which is much *less* than the experimental value of  $C$  at  $120^{\circ}\text{C.}$  It seems reasonable to infer that the assumed type of solution is *impossible*, and that the lines of constant  $H$  cannot be straight lines. Still less is it possible that they should have a slope diminishing with fall of  $T$  and  $P$ , as shown by Peake's lines E and F (Fig. 10).

The second assumption,  $C = F(T)$ , as already remarked, can be made to give very fair agreement with experiments between  $120^{\circ}$  and  $180^{\circ}\text{C.}$  It remains to show that it also gives quite reasonable values of  $H$ , with certain limitations, when extrapolated to the critical point. Taking the simple assumption  $C = K/T^n$ , it follows, from the expression already given for  $H - B$ , that when  $H = B$ , and  $(n + 1) CP/T = 1$ ,  $S$  becomes infinite, and  $(dH/dT)_c$  also becomes infinite, but with a negative sign, provided that  $C (dp/dT)$  is greater than 1. The last condition is satisfied if  $n \mp 1$  does not exceed  $(T/p) (dp/dT)$ , the value of which is 7.18 at  $374^{\circ}\text{C.}$  according to the formula assumed for  $p$ . Since the variation of  $H_c$  near the critical point is extremely rapid, it is unnecessary to know the values of  $B$  or  $h$  or  $p$  with great accuracy. Proceeding in this way we find that the values  $C_{100} = 0.405$ , and  $n = 4.25$ , satisfy the condition  $H = B$  at the critical point, in addition to giving very fair agreement with observed values of  $C$  between  $120^{\circ}$  and  $180^{\circ}\text{C.}$

The following table shows values of  $H_c$  calculated by the formulae

$$C = F(T) = 0.405 (373.1/T)^{4.25}; \dots\dots\dots(20)$$

$$H - B = S_0 T (1 - 5.25 Cp/T)^{1/5.25}, \dots\dots\dots(21)$$

for comparison with values obtained from the formula of the Thiesen type with  $t_c = 374^{\circ}\text{C.}$ , (19) in Chap. II, previously employed, and with values given by the author's original assumption  $SC = F(T)$ , as embodied in the Steam Tables. The latter formula, as already explained, is of an unsuitable type for extrapolation beyond  $250^{\circ}\text{C.}$ , but is the simplest and most convenient to employ at ordinary temperatures in practice. The same value of  $H_c$  at  $100^{\circ}\text{C.}$ , namely 639.8, is assumed in each case, and the same values of  $S_0$  and  $p$ . The value assumed for  $S_0$  does not affect the

values of  $L$  obtained from formula II (19), but the values of  $H$  deduced depend to a small extent on those of  $dp/dt$  owing to the term  $avT(dp/dt)$  in the author's expression for  $h$ , which is used in deducing  $H$ , from  $L$ .

It will be seen that the two assumptions,  $C = F(T)$ , and  $SC = F(T)$ , give identical results to 0.1 caloric between 100° and 200° C. They also give equally good agreement between 0° and 100° C. Both differ slightly over this range from the empirical formula, but the difference is less than 1 in 1000, and much smaller than the discrepancies of experimental measurements of  $H$ . Beyond 200° C. the assumption  $C = F(T)$  gives slightly lower results than formula II (19), though both tend to the same limit  $H = B$  at 374° C.

The values assumed for  $p$  begin to be uncertain at 250° C., but make little difference at this point. Thus if we take  $p = 565.6$  in place of 575.7, the value of  $H$  for  $C = F(T)$  is raised to 679.0 in place of 678.0, and that for  $SC = F(T)$  is raised from 679.5 to 680.1 as given in the Steam Tables. The formulae diverge more rapidly at higher temperatures. The assumption  $C = F(T)$  is probably to be preferred in the neighbourhood of the critical point, but the experimental evidence appears to be rather in favour of  $SC = F(T)$  at ordinary temperatures, because it gives better values of the volume. It could hardly be expected that any such simple assumption as  $C = F(T)$ , or  $SC = F(T)$ , would represent all the properties of steam accurately over the whole range from 0° to 374° C. But the fact that the two assumptions agree so closely from 0° to 250° C. may be regarded as corroborating the variation of  $H$  previously given, and as showing that the truth probably lies between the two formulae, which cannot easily be distinguished by experiments on  $C$  or  $H$  over the restricted range available in practice.

Table V. Values of  $H$ , for  $C = F(T)$ .

Temp. Cent. °	120°	140°	160°	180°	200°	250°	300°	350°
$C = F(T)$	647.1	654.2	660.6	666.2	671.0	678.0	674.6	646.4
$SC = F(T)$	647.1	654.2	660.6	666.2	671.0	679.5	—	—
II (19)	646.9	653.8	660.2	666.0	671.0	680.0	679.7	649.7

In order that the solution found for the case  $C = F(T)$  should be completely consistent, it is also necessary that the values of the volume deduced from those of  $H$  by Clapeyron's equation, should



agree with those deduced from the corresponding form of characteristic equation, namely,

$$aPV/RT_c = 1 - S_0/5.25R + (H - B)/5.25RT_c. \dots(22)$$

This equation gives a value of the critical volume  $V_c = 0.0884$  agreeing as closely as can be expected with the value  $v_c = 0.0892$  for the liquid deduced from the expression for  $h$  on the assumption that  $h_c = 464$ . The agreement in the values of  $V$  is also good between  $100^\circ$  and  $200^\circ$  C., but is not so good at points between  $250^\circ$  and  $350^\circ$  on account of the uncertainty of  $p$  and  $dp/dt$ . Thus at  $250^\circ$  C. the value of  $V$  obtained from the characteristic equation (22) with  $p = 575.7$  as given by the empirical formula (19), is 0.8576, but the value from Clapeyron's equation is only 0.8154. Better agreement is obtained if the author's theoretical equation for  $p$  is adopted, with  $p = 565.6$  and  $dp/dt = 9.210$  (F.P.C.). These give, from the characteristic equation  $V = 0.8761$ , and from Clapeyron's equation  $V = 0.8674$ . The value of  $p$  required for complete agreement is approximately 563 lbs., giving  $V = 0.881$ . Generally speaking, the simple assumption  $C = K/T^n$ , with any possible values of  $K$  and  $n$ , satisfying the condition  $(n + 1) Cp/T = 1$  at  $374^\circ$  C., requires somewhat lower values of  $p$  between  $250^\circ$  and  $350^\circ$  C. than those given by (19) or commonly assumed.

If equation (22) is corrected for  $b$ , as indicated in the footnote p. 78, we find  $V_c = 0.0507$ ,  $h_c = 491$ , agreeing closely with Table X, Chapter VIII. But there is strong evidence that  $C$  cannot be a function of the temperature only at very high densities near the critical point. Thus in the case of  $\text{CO}_2$  at its critical temperature,  $31.5^\circ$  C., the cooling-effect is nearly independent of  $P$  and equal to  $0.070^\circ/\text{lb.}$  at moderate pressures, but it falls sharply to  $0.0488$  at the critical pressure of 1070 lbs., and diminishes rapidly to a still smaller value for higher densities at the same temperature.

## CHAPTER V

### THE SPECIFIC VOLUME OF STEAM

**42. Experiments previous to 1900 on the Specific Volume of Steam.** On account of surface condensation and of the presence of floating particles of liquid, the older measurements of the density or specific volume of *saturated* steam (such as those of Fairbairn and Tate, *Phil. Trans.* 1860, p. 185) led to such irregular results that it has generally been considered preferable to deduce the specific volume in the state of saturation from Clapeyron's equation, II (7). The essential point, however, is to make the values of the specific volume thermodynamically consistent with those of the latent heat, which could also be done by deducing the values of the latent heat from those of the specific volume in the state of saturation, provided that the specific volumes and  $(dp/dT)$  could be measured satisfactorily. The objection to this method is that the *deviation* of the total heat or latent heat from lineality, as shown by the expressions already given, depends chiefly on the small defect of volume  $(c - b)$  from the ideal volume  $RT/aP$ , and not on the whole quantity measured. The great advantage of the Joule-Thomson, or throttling method, is that it gives the *variation* of total heat directly in terms of the specific heat, and that the corresponding deviations of volume  $(c - b)$  can also be deduced with great accuracy. Clapeyron's equation then becomes available for determining the values of  $(dp/dT)$  with greater precision than is possible from observations of  $p$  itself. Direct measurements of the latent heat (except at  $100^{\circ}\text{C.}$ ) and specific volume are not theoretically required, but are useful as an independent check on the results.

Among the best results for the specific volume previous to 1900 were those of Battelli (*Mem. Accad.*, Turin, 1893, 43, p. 63). Tumlrz (*Sitz. Akad. Wiss.*, Vienna, 1899, p. 1058) showed that Battelli's results could be represented within the limits of experimental error by taking the defect of volume  $(c - b)$  to be constant. Grindley (*Phil. Trans.*, 1900) deduced a similar equation from his throttling experiments, assuming Regnault's linear formula for

the variation of the total heat. But his experiments were otherwise inconsistent with the formula of Tumlirz, as already explained (Chap. IV, § 85), and the value found for the constant defect of volume was quite different.

Grindley's constant value of the defect of volume was about 11 times larger than that given by the equation of Tumlirz, and would fit fairly well with the curves of constant  $H$  on the  $PT$  diagram, in the neighbourhood of  $130^{\circ}\text{C}$ ., if the specific heat were constant and equal to 0.48. But it would make the defect of volume from the ideal nearly five times too large in this region. Linde has proposed an equation of a similar type with the value of the constant 0.016 cb. m./kg., "as being suitable for most practical calculations." This would make the defect of volume about right at  $150^{\circ}\text{C}$ ., but would make the cooling effect nearly five times too small. It would also require that  $S$  should be a function of the temperature only, and would give impossible values of  $H$  or  $S$ .

**43. Zeuner's Equation.** The equation for the volume most commonly employed in 1900, and still very often used at the present time, is that of Zeuner, quoted as equation (1) in the last chapter. We have already seen that this equation is of an unsuitable type to represent the lines of constant  $H$ , or the cooling effect, since it makes  $C$  infinite at zero pressure, and much too small at high pressures. But it is otherwise of a very convenient type for practical purposes. Zeuner realised very clearly the practical importance of making the equation as simple as possible and exactly consistent with an adiabatic of the type  $P/T^n = K$ . His form of the equation was chosen to fit with the adiabatic  $P/T^4 = K$ , and to give a constant value 0.4805 for the specific heat at constant pressure. Unfortunately this requires the high value

$$0.4805 \times 424/4,$$

or 50.933 for the constant  $R/A$ , which is 8 per cent. greater than that corresponding to the molecular weight, and therefore extremely improbable.

By choosing the coefficient of  $P^{\frac{1}{4}}$  in the last term, namely  $192.5P^{\frac{1}{4}}$ , to make the volume of saturated steam at  $100^{\circ}\text{C}$ . equal to 1.650 cb. m. (the value deduced from Regnault's formulae for the latent heat and  $dp/dt$ ) the equation was found to give very fair agreement with Regnault's values for the total heat and the

volume of saturated steam over a considerable range of temperature. This agreement is illustrated in the following table, in which the author's values are also included for the sake of comparison.

Table I.

Values of  $H$  and  $V$  by Zeuner's Equation compared with Regnault.

Temp. Cent.	Total Heat $H$ , in Calories C.			Volume $V$ , in cubic metres per kg.		
	Regnault	Zeuner	Callendar	Regnault	Zeuner	Callendar
0°	606.5	602.2	594.3	210.7	213.7	204.5
20°	612.6	609.7	603.7	58.73	59.80	57.57
40°	618.7	617.0	613.0	19.67	20.00	19.51
60°	624.8	623.9	622.2	7.654	7.742	7.674
80°	630.9	630.6	631.0	3.379	3.396	3.408
100°	637.0	637.0	639.3	1.650	1.650	1.672
120°	643.1	643.3	647.1	0.8753	0.8740	0.8907
140°	649.2	649.4	654.2	0.4977	0.4971	0.5083
160°	655.3	655.3	660.6	0.3001	0.3003	0.3073
180°	661.4	661.3	666.1	0.1901	0.1913	0.1952
200°	667.5	667.0	671.0	0.1257	0.1274	0.1295

The simplest method of deducing the formula for  $H$  from Zeuner's equation is to observe that, since the equation satisfies the condition for the adiabatic  $P/T^4 = K$ , we must have

$$H = 4aPV + B,$$

where  $a = 1/424$  according to Zeuner's units, and  $B = 476.1$  to give  $H = 637$  at  $100^\circ \text{C}$ .

The ideal volume at  $0^\circ \text{C}$ . deduced from the molecular weight of steam, is approximately 205.0, which is much smaller than Regnault's 210.7. Zeuner's value is still higher. This might have been explained by supposing (with Kirchhoff) that steam at low pressures did not obey Avogadro's law, if it were not that Dieterici's and Griffiths' values of the latent heat are conclusive evidence to the contrary.

Regnault's values of the volume from  $20^\circ$  to  $60^\circ \text{C}$ . agree better with the author's equation than with Zeuner's. Above  $100^\circ \text{C}$ ., Regnault's values are all too low, but agree very closely with Zeuner's equation from  $80^\circ$  to  $180^\circ \text{C}$ .

If the ideal volume is represented by Zeuner's expression  $50.933 T/P$ , the defect of volume, represented by  $192.5P^{-\frac{1}{2}}$ , exceeds 10 per cent. of the ideal at  $100^\circ \text{C}$ ., but increases rapidly with diminution of pressure at constant temperature, instead of re-

remaining nearly constant, as in the case of normal gases and vapours, for which the defect of volume is found to be a function of the temperature only to a first approximation. If, on the other hand, the ideal volume is taken to be that corresponding with Avogadro's law, namely  $47T/P$ , as in Fig. 11, the defect of volume according to Zeuner for saturated steam at  $100^{\circ}\text{C}$ . is only 2.8 per cent., which is still nearly double that required by recent measurements of the latent heat and saturation pressure. The defect of  $V$  vanishes, and the vapour becomes "pluperfect," when  $T = 49P^{\frac{1}{2}}$ , i.e. at about  $220^{\circ}\text{C}$ . for steam at atmospheric pressure. This behaviour is so inconsistent with all molecular theory that the agreement of Zeuner's equation with Regnault's experiments cannot be regarded as otherwise than an accidental coincidence due to an empirical adjustment of constants.

When tested by comparison with later measurements of the volume or total heat, Zeuner's equation necessarily shows the kind of disagreement to be expected from the known errors of Regnault's experiments. This point is illustrated in Fig. 11 by the dotted lines representing the percentage defect of volume from Avogadro's law according to Zeuner's equation, for the saturation line, and for  $V = 1.6$ . The defect from Zeuner's own ideal volume  $50.9T/P$ , could not be shown in the figure as it would lie entirely outside the page. It will be seen that the saturation line is nearly straight but has the wrong curvature, the percentage defect from  $47T/P$  increasing at first too rapidly, but at a rate diminishing instead of increasing with increase of pressure and temperature. Similarly, the line of constant volume,  $V = 1.6$ , does not correspond at all with the points representing the observations at that volume, but gives nearly double the observed defect, approaching closely to line No. 11, with  $V = 0.825$ , in place of No. 1, with  $V = 1.598$ .

**44. The Munich Experiments on  $V$ .** The best experiments hitherto recorded on the specific volume of *dry* steam, appear to be those of O. Knoblauch, R. Linde, and H. Klebe (*Forsch. Ver. Deut. Ing.* 21, 1905) made at the Munich laboratory with apparatus provided by C. Linde. They employed a modification of the method of Fairbairn and Tate. A known mass of water in a glass vessel, with a vertical stem containing mercury and serving as one limb of a manometer, is heated externally by steam at a suitable pressure. The volume is known from preliminary calibration, with small corrections for expansion and compression, previously determined.

The pressure and temperature are directly observed. The results of Fairbairn and Tate were limited to the immediate neighbourhood of the saturation point, and were probably vitiated by errors of surface condensation due to chemical action of the steam on the glass. Ramsay and Young at a later date found large errors from this cause in their experiments on steam. The Munich observers endeavoured to minimise this source of error by employing a large bulb of special glass for the containing vessel, and deduced the saturation volume, in the same way as Battelli, by extrapolation from the observations at a moderate degree of superheat. The observations for each filling of the bulb gave the variation of pressure with temperature for a constant mass of steam at nearly constant volume. By plotting the pressure against temperature for each filling, they found the lines of constant volume on the  $P, T_v$  diagram to be straight lines within the limits of error of their experiments. They obtained the values of the saturation volumes by extrapolating these lines to the saturation curve, and they deduced the corresponding  $PV$ ,  $P$ , or "Amagat" diagram, by observing the points of intersection of these lines with lines of constant temperature, and plotting the isothermals on the Amagat diagram with the values of  $PV$  thus obtained. This graphic process of smoothing involves the tacit assumption that  $P$  is a linear function of  $T$  at constant volume, which is well known to be untrue in the case of any other gas or vapour, and may introduce systematic errors. It follows that the  $PV$ ,  $P$  diagram of Linde, which is commonly quoted and reproduced, does not directly represent the original observations. The lines of constant temperature, instead of being very nearly straight, as they should be at low pressures, show an appreciable curvature which may be attributed in part at least to the process employed in deducing the diagram.

The author's form of characteristic equation

$$V = 47T/P - 0.0263 (373/T)^{1/2} + 0.0010, \dots\dots\dots(1)$$

has been described as "grossly inaccurate," because it makes the isothermals straight lines on the Amagat diagram (which is known to be a very good approximation in the case of normal gases and vapours), and because it does not exactly satisfy the condition assumed by Linde in smoothing the observations, namely that  $P$  is a linear function of  $T$  at constant volume. As a matter of fact the Munich observations cannot be represented by any equation satisfying this condition, and it is a sufficient answer to this objec-

tion that the equation calculated by Linde himself to represent the Munich experiments as closely as possible, namely

$$V = 47.10T/P - (1 + 0.000002P)(0.681(373/T)^3 - 0.0052), \dots (2)$$

does not make the lines of constant volume straight on the  $P, T$  diagram, but is a slight modification of the author's equation\*. The small factor depending on  $P$  was introduced by Linde to represent the curvature of the isothermals on the Amagat diagram, which results partly from the assumption made in smoothing the observations. Linde himself states that the Munich observations, though quite irreconcilable with the equations of Zeuner or Tumlirz, are represented "with great accuracy" up to  $160^\circ \text{C.}$  by the author's equation. This is the more remarkable because he quotes the original form of the equation (*R. S.*, 1900) with Maxwell's theoretical value of the index  $n = 3.5$ , in place of the experimental value  $n = 10/3$  given in the revised equation (*E. B.*, 1902) which represents the actual observations much more closely. It is not to be expected that an equation of the simplest possible type, deduced from observations of the specific heat, cooling-effect, and adiabatic index, should represent a *later* series of observations on the volume with the same degree of accuracy as a more complicated equation specially calculated for the purpose. But the agreement of the author's equation with the Munich observations is far closer than would be inferred from an inspection of Linde's diagram, and is of such a kind as to suggest that the modifications introduced by Linde may be largely due to errors of surface condensation, and to distortion involved in the process of smoothing. In order to make a fair comparison, it is necessary to eliminate the assumption that  $P$  is a linear function of  $T$  at constant volume, and to go back to the actual observations themselves. Much better agreement is thus obtained. It is also necessary to plot the observations on a much larger scale than in Linde's diagram in order to exhibit the nature of such small discrepancies as exist between them.

**45. Reduction of the Observations.** Since  $P, V$ , and  $T$  are the quantities actually observed, the most direct method of testing the consistency of the observations and exhibiting their agreement with the formula, is to calculate the value of  $\alpha PV/T$  for each observation and compare it with the constant  $R$ . The small differences may then easily be plotted on a scale sufficiently large

\* Equations (1) and (2) give  $V$  in  $\text{cb. m./kg.}$  when  $P$  is in  $\text{kg./sq. m.}$

to show both the experimental errors and the deviations from the formula. Or the values of  $R$  at each point may be calculated by adding to the value of  $aPV/T$  the value of the difference  $a(c-b)P/T$  according to the author's formula. With the exception of filling No. 10, which gives discrepancies of 1 per cent. the values of  $R$  thus found are remarkably concordant for the observations taken with any one of the 32 fillings. But they vary from one filling to another under similar conditions in an irregular manner which is evidently due to errors in the determination of the mass of water introduced into the globe. Thus the value of  $R$  from No. 4 is 0.6 per cent. too high, and that from No. 7, 0.8 per cent. too low. These excessive errors occur chiefly in the short lines near the saturation point, where the range of temperature covered is too small to give the observations any value for verifying the formula. Of the long lines covering an extended range of temperature, the greatest differences are 0.3 per cent. between 1 and 5, and 0.24 per cent. between 5 and 12 in the opposite direction. In order to eliminate these accidental differences as far as possible from the comparison, the value of the mass for each filling has been corrected to the same mean value of  $R$ , namely 0.11012, in terms of the mean thermal unit. It happens that this value is almost exactly the mean of all the values of  $R$  calculated from the separate observations, excluding a few obvious experimental errors. It is very natural that such accidental errors should occur in the values of the mass of water introduced into the bulb, because the introduction involved some very difficult experimental manipulation, including scrupulous cleaning, drying, freezing with solid  $\text{CO}_2$ , and evacuating. In the first few fillings the whole mass introduced was less than 2 grams, and errors of a few milligrams were inevitable. The largest correction applied to the mass of this account is only 1 in 400 in the case of filling No. 1 (where the whole mass was about 1.5 gm.), and is equivalent to an error of 4 mgm.

The quantity plotted in the diagram Fig. 11, the scale of which is about ten times as large as Linde's  $PV, P$  diagram, is not the whole volume but only the defect of  $aPV/T$  from the ideal value  $R$ , plotted as a percentage of  $R$ . The actual observations are shown by the small circles in relation to the lines of constant volume given by the author's formula.

The ordinate corresponding to each circle represents the difference  $1 - aPV/RT$ , multiplied by 100, as calculated directly from the Munich tables of observations. The crossed circles repre-



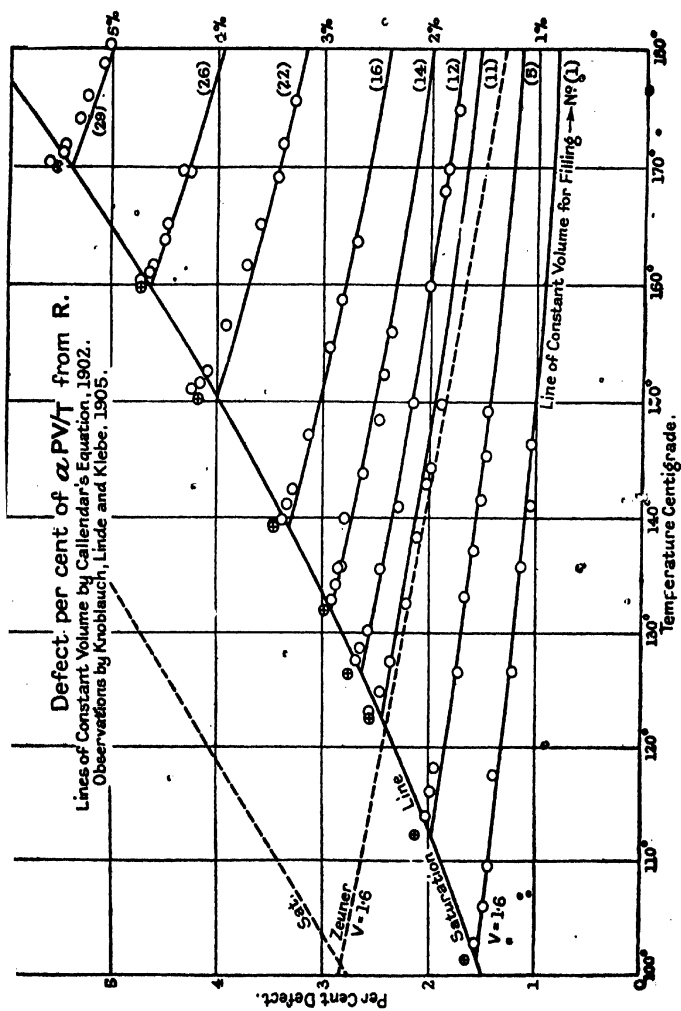


Fig. 11.

sent the extrapolated values at saturation given in the same tables. The lines of constant volume represent the corresponding quantity, namely  $100(c - b)/(V + c - b)$ , according to the author's formula. This is very easily calculated by the aid of the table of values of  $c$  for each degree given in the Steam Tables, Appendix III. The agreement is seen to be almost incredibly perfect, since each point represents a single observation, and not the mean of a group. The deviations rarely amount to 1 in 1000, except in the case of the observations near the saturation line, which are obviously vitiated by surface condensation, as the observers themselves admit. For this reason the short lines, in which the observations extended only a few degrees from the saturation point, could not be included in the diagram without confusion, because many of them exhibit much larger effects of surface condensation than any shown in the figure.

It appears probable that the effect of surface condensation in increasing the percentage deviation near the saturation point, depends partly on accidental traces of dirt or impurity, and partly on the chemical action of the water on the glass, which increases rapidly with rise of temperature and pressure. The effect of any dissolved impurity is to lower the vapour pressure or raise the boiling point, so that some liquid remains when the temperature is above that of saturation. In the case of water the rise of boiling point produced by  $x$  gram-molecules of salt in solution per gram of water is approximately  $1000x$  degrees C. The proportion of water remaining when the temperature is  $\theta^\circ$  C. above the saturation point will therefore be  $1000x/\theta$ . Thus the defect of  $pv$  due to surface condensation should be represented by a hyperbolic curve, as is easily seen to be the case for filling No. 22, where the effect is well marked. The effect may extend for 10 or more degrees beyond the saturation point, depending on the temperature at which the solution becomes saturated, and is not limited to  $1^\circ$  or less as the observers supposed. The observations indicate clearly that the correction they applied for surface condensation was inadequate, and that all the saturation points are liable to a small systematic error. For No. 22 the defect of volume due to surface condensation may be estimated at 2 in 1000 for  $\theta = 2.5^\circ$ . The impurity required to produce this effect would be only 5 millionths of a gram-molecule of salt per gm.

Above  $180^\circ$  C. there are only three short lines, which show deviations reaching 0.7 per cent. from the formula, but the observa-

tions are so few, and the experimental difficulties increase so rapidly with the pressure, that little weight can be attached to them. The observers themselves do not tabulate their general results beyond 180° C., and though some deviation is to be expected at higher pressures, it is impossible to say how far the deviation shown is due simply to increasing experimental errors. The author's formula agrees very well with the saturation pressures up to 200° C.; and it would be undesirable to introduce any modification to suit these few observations between 180° and 190° C. without much more conclusive experimental evidence.

**46. Comparison of Formulae for  $V$  and  $L$ .** The agreement of Linde's formula with the author's in the neighbourhood of the saturation curve is much closer than would be imagined from a mere comparison of the constants, and is within the limits of probable error of the method. The differences become serious only when the formula is extrapolated to high temperatures or pressures, beyond the limits of the experiments themselves. The agreement in the neighbourhood of saturation is illustrated by the following table, in which Henning's values calculated from his smoothed table of  $L$ , are included for comparison.

Table II. Volume  $V$ , and Latent Heat  $L$  of Saturated Steam.

Temp. Cent.	$V$ in litres per kilogram			$L$ in calories Centigrade		
	Callendar 1902	Linde 1905	Henning 1909	Callendar from $S \& C$	Linde from $V$	Henning Table
100°	1672.2	1675.5	1673	539.3	538.7	538.7
110°	1200.1	1210.8	1210	533.2	532.0	532.1
120°	800.7	892.2	891.2	526.9	525.5	525.3
130°	667.6	669.0	667.5	520.3	518.7	518.2
140°	508.3	509.0	507.8	513.6	511.5	510.9
150°	392.6	393.2	392.1	506.6	504.2	503.8
160°	307.3	307.2	307.1	499.3	497.0	496.6
170°	243.5	243.0	243.0	491.8	489.7	489.4
180°	195.2	194.3	194.7	483.9	482.3	482.2

Henning's values of the volume agree on the whole better with the author's than with Linde's. Linde's high values from 100° to 150° C. are due chiefly to the high value 47.10 selected for the constant  $R/a$ . So high a value of this constant was not justified by the actual observations on the volume, which give  $R = 46.99$ .

but was required to compensate for the exceptionally low values of  $dp/dt$  in the neighbourhood of  $100^\circ \text{C.}$  deduced from the Munich observations on the saturation pressure, since it had been shown by the reduction of Joly's observations (*R. S.*, 1900) that the latent heat at  $100^\circ \text{C.}$  could not well be much lower than 539 in terms of the calorie at  $15^\circ \text{C.}$  as previously explained. The values of the saturation pressure itself, and *a fortiori* those of  $dp/dt$ , could not be determined very satisfactorily from the Munich observations, especially near the limits of the experimental range at  $100^\circ$  and  $180^\circ \text{C.}$ , because the mercury thermometers employed showed irregularities of  $0.1^\circ$ , equivalent to nearly 20 mm. in the saturation pressure at the highest points, with an even larger proportionate uncertainty in  $dp/dt$  for the lower ranges. The fact that the values of the latent heat calculated by Linde agree so well with those subsequently found by Henning, is a most remarkable coincidence. The differences nowhere exceed 1 in 1000, and are much smaller than the probable error of the calculation as estimated by Henning himself. But we have already seen that Henning's table does not represent his actual observations satisfactorily, and the coincidence merely shows that there must be systematic errors in the values of  $dp/dt$  (see p. 144) if the values of the volume are correct.

Henning's table of latent heat makes the rate of diminution of  $L$  discontinuous near  $100^\circ$ , but practically constant and equal to  $0.72$  calorie per  $1^\circ \text{C.}$  from  $120^\circ$  to  $180^\circ \text{C.}$ , which is theoretically impossible. The curve of latent heat must obviously be continuous with the well established curve below  $100^\circ \text{C.}$ , and the rate of diminution with rise of temperature must increase more rapidly as the temperature rises, as shown in the author's table representing values calculated from the theoretical expression

$$(H - st)(1 - v/V),$$

which gives

$$L = [594.3 - (s - S_0)t - SCp](1 - v/V). \dots\dots(3)$$

The constant 594.3 is the value of  $L + SCp$  at  $0^\circ \text{C.}$  The factor  $(s - S_0)$  is the difference of the limiting specific heats of liquid and vapour, representing the primary cause of variation of the latent heat. The term  $SCp$ , which increases rapidly with the saturation pressure  $p$ , represents the Joule-Thomson effect and becomes important at temperatures above  $100^\circ \text{C.}$  The factor  $(1 - v/V)$  shows that the latent heat vanishes when the volume of the liquid  $v$  becomes equal to that of the vapour  $V$ . This formula for  $L$  is the

simplest possible, and is exactly consistent with Clapeyron's equation, and with the characteristic equation for the volume. It is quite possible that the rate of diminution of the latent heat may increase more rapidly with temperature above  $200^{\circ}\text{C}$ ., than is shown by the simple term  $SCp$ , and the factor  $(1 - v/V)$ . But the properties of *saturated* steam at temperatures above  $200^{\circ}\text{C}$ . are of little practical importance, and no satisfactory experimental data exist at present for the volume, or the latent heat, or the specific heat, or the cooling-effect in this region. The author's formulæ are intended for practical use over the experimental range, and it would be a great mistake to spoil them for practical purposes by introducing purely speculative complications devised to suit the possible behaviour of the saturated vapour at higher temperatures. The pressure factor  $(1 + 0.000002p)$  in Linde's equation is a device of this type, which is to be deprecated as an unnecessary complication at low pressures, besides giving impossible values for  $H_g$  at high pressures (see p. 122), as explained in the next chapter. There are other serious objections to Linde's equation which cannot be passed over, because his formula has been so widely adopted, as being the most accurate for *superheated* steam, which is quite contrary to the experimental facts.

**47. Objections to Linde's Equation.** The correction term  $0.031 (373/T)^3 - 0.0052$ , in Linde's equation vanishes and changes sign at  $t = 402^{\circ}\text{C}$ . a few degrees above the critical point. According to Linde's equation, steam becomes a "pluperfect" gas above this temperature, deviating from Boyle's law in the same way as hydrogen, the product  $PV$  increasing with increase of pressure at constant temperature instead of diminishing, which cannot possibly be correct. The reason of this is chiefly that Linde has assigned too high a value to the constant 0.0052 (which is more than five times as great as in the author's equation) in order to compensate for the selection of the lower value 3 for the index in place of the author's  $10/3$ . The excuse given for this is merely the convenience of having a whole number for the index. It will be found however that the index  $10/3$  is in many respects more convenient than the index 3 in actual practice having regard to all the various calculations for which it is required, more particularly in relation to the adiabatic equation, which Linde appears to have overlooked. It may be argued that a temperature of  $400^{\circ}\text{C}$ . is so seldom reached in a steam-engine that the error is immaterial.

It is evident however that material discrepancies may be expected long before this temperature is attained.

It is most important in practice, for calculations relating to the discharge of steam, and for other reasons, to have the simplest possible form, like the author's  $P/T^{n+1} = K$ , for the adiabatic equation. To be of any use, the results of such calculations must be exactly consistent with the tables. Linde's equation does not satisfy the theoretical condition (14) of Chapter III, namely that the deviation from the ideal volume must be of the form

$$(T/P) F (P/T^{n+1}).$$

It is therefore extremely inconvenient in practice; in addition to being almost certainly inaccurate at high temperatures.

The measurements of the volume taken alone were inadequate to determine all the constants in the equation, since the observations of  $V$  might have been represented equally well by a variety of other formulae of different types. The values of the constants were accordingly adjusted as far as possible to suit other observations, such as those on the cooling-effect. But in spite of the complexity of the equation the agreement obtained is not at all satisfactory, and the formula cannot be reconciled with observations on the specific heat as will be explained in the next chapter.

## CHAPTER VI

### THE SPECIFIC HEAT OF STEAM

**48. Variation of the Specific Heat.** The experimental and theoretical evidence leading to the adoption of the formula (*R. S.*, 1900)

$$S = S_0 + an(n+1)cP/T, \dots\dots\dots(1)$$

for the variation of the specific heat of steam at constant pressure, has already been summarised and explained in Chapter III, and the formula itself has been indirectly verified by the comparison of the resulting values of the total heat, cooling-effect, and specific volume, with those obtained by experiment. It remains in the present chapter to complete the verification by direct comparison with the results of later experiments on the specific heat, and to discuss some of the thermodynamical relations, which afford good illustrations of the application of the laws of thermodynamics to test the consistency of various empirical expressions which have since been proposed.

The limiting value of the specific heat  $S_0$  at zero pressure is a function of the temperature only, and has been taken as constant for the range required in steam-engine practice, although it might theoretically be any function of the temperature so far as the form of the characteristic equation for  $V$  in terms of  $P$  and  $T$  is concerned. Recent experiments have shown that the value of  $S_0$  is not quite constant over the experimental range, and that the variation becomes important at temperatures approaching  $2000^\circ\text{C}$ ., such as commonly occur in internal combustion engines. But it has been found possible to represent the properties of steam satisfactorily up to a temperature of  $400^\circ\text{C}$ . by adopting a suitable mean value of  $S_0$ . This appears to be justifiable because the uncertainty of the variation of  $S_0$  over this range according to different experiments and formulae is nearly of the same order of magnitude as the variation itself. Moreover it is most important for practical calculations on the discharge of steam, and for other purposes, that the equation of the adiabatic of dry steam should be of the simplest possible form, namely  $P/T^{n+1}$ , and should be exactly consistent with the

tables. This cannot be secured unless a constant value is assumed for  $S_0$  over the experimental range, and is a decisive argument in practice.

As the result of extended trials in various calculations of the properties of steam from experimental observations and tests, it has not hitherto been found possible to make any material improvement in the value  $13R/3$ , assumed for  $S_0$  in the revised equations (*E. B.*, 1902). This value has accordingly been retained in order to avoid introducing immaterial and vexatious changes in the Steam Tables. It is probable that this value is too high near  $100^\circ\text{C}$ ., where Makower found values ranging from 4.26 to 4.30 for the ratio  $S_0/R$ , and where Brinkworth has recently obtained the value 4.21. But a higher value is certainly required at  $200^\circ$  than at  $100^\circ\text{C}$ ., and the value 4.333 seems to give the best general agreement with the latest observations of the saturation pressure as explained in a later chapter.

The second term in formula (1), which depends on  $P$ , and may be called the variation with pressure, is of much greater magnitude and importance than the variation of  $S_0$ . Its presence in the formula is essential in order to make the values of the specific heat thermodynamically consistent with the variation of the total heat, volume, and saturation pressure.

**49. Results of Later Observers.** The approximate constancy of the specific heat of steam at atmospheric pressure was verified indirectly by the experiments of Holborn and Henning (*Ann. Phys.*, 18, p. 739, 1905), which covered a wide range of temperature. They employed a modification of Regnault's method with an oil calorimeter at  $110^\circ\text{C}$ ., so that the steam was not condensed in the calorimeter, and the possible error due to the inclusion of the latent heat was avoided. They also measured the specific heat of air with the same apparatus over the same ranges of temperature. The value found for air between  $110^\circ$  and  $270^\circ\text{C}$ . was 0.2815, and that for steam over the same range, 0.4492. They admitted that these results were too low as compared with those of Regnault, but they considered that their experiments gave the ratio of the specific heats of steam and air with a fair degree of accuracy, and that the variation of the mean specific heat of air with temperature could be fairly represented by the coefficient  $4 \times 10^{-5}$ . At a later date, Swaine (*Brit. Assoc. Rep.*, 1908, p. 81, *Phil. Trans. A*, 1910, p. 199) found a similar coefficient for the rate



of increase of the mean specific heat of air between  $0^{\circ}$  and  $100^{\circ}$  C., but a much higher value of the specific heat itself, namely 0.2418 at  $0^{\circ}$  C. and 0.2423 at  $100^{\circ}$  C. These exceeded Regnault's values by 2 per cent., but agreed very closely with Joly's observations on the specific heat at constant volume when reduced to constant pressure.

Swann's result for air has since been verified by Holborn and Jakob (*Zeit. Ver. Deut. Ing.*, 58, p. 1429, 1914). The original results of Holborn and Henning for steam can be reduced, with a fair degree of probability, by employing Swann's formula for the mean specific heat of air, together with their own values of the ratio air/steam. The results thus obtained are exhibited in the following table (*Brit. Assoc. Rep.*, 1908, p. 31).

Table I. Reduction of Holborn and Henning's Values for  $S$ .

Temp. } Range }	$110^{\circ}$ 270°	$110^{\circ}$ 440°	$110^{\circ}$ 620°	$110^{\circ}$ 820°	$115^{\circ}$ 826°	$270^{\circ}$ 440°	$440^{\circ}$ 620°	$620^{\circ}$ 820°
Mean $t$	$190^{\circ}$	$275^{\circ}$	$365^{\circ}$	$465^{\circ}$	$470^{\circ}$	$355^{\circ}$	$530^{\circ}$	$720^{\circ}$
Air, obs.	0.2315	0.2350	0.2442	0.2492	—	0.2382	0.2612	0.2618
Steam, obs.	0.449	0.460	0.475	0.498	—	0.470	0.503	0.556
Ratio	1.940	1.958	1.946	1.998	1.900	1.974	1.924	2.122
Air, calc.	0.2445	0.2457	0.2471	0.2487	0.249	0.2468	0.2497	0.2528
Steam, calc.	0.474	0.481	0.481	0.497	0.473	0.487	0.480	0.536

The calculated values given in the last line agree very fairly with Regnault at  $173^{\circ}$  C., but indicate a much smaller rate of increase with temperature than the original observations given in the fifth line, headed Steam, obs. The observations for the range  $115^{\circ}$  to  $826^{\circ}$  in the fifth column were taken with a different form of apparatus, which gave a much lower result than the first form over the same range, but the experimental difficulties were so great at these temperatures that little weight can be attached to it. The values given in the last three columns are deduced by taking differences of total heat between the first four ranges, and show the values of  $S$  over smaller ranges and at higher temperatures. The uncertainty is increased by taking differences in this way, but the results indicate a more rapid increase at high temperatures, as is also shown to be the case by explosion experiments. The calculated values shown in the last line are probably too low at higher temperatures, because it appears likely that the specific heat of air may increase more rapidly in this region than is assumed in the formula. Even the value 0.474 at  $190^{\circ}$  may be 1 or 2 per cent. too

low from this cause, and should be regarded rather as a lower limit to the possible value of  $S$ .

**50. Variation of  $S$  with Pressure:** According to the theory already explained, it is not actually necessary to take any observations of the specific heat at pressures other than atmospheric, because the complete variation of the total heat is most easily deduced by the throttling method when the specific heat at atmospheric pressure is known. The advantage of this method is that the observation of the cooling-effect is much simpler than that of the specific heat, because no measurements of quantities of heat are required. Moreover measurements of the specific heat at pressures other than atmospheric involve additional experimental difficulties and sources of error. It is of considerable interest, however, to compare measurements at different pressures with the results deduced from the observations on the cooling-effect.

The variation of the specific heat with pressure as deduced from the observations on the cooling-effect, is shown by the full lines in the annexed diagram (Fig. 12), which are drawn for pressures of 0, 2, 4, 6, and 8 kilos per sq. cm. in accordance with equation (1) for the variation of  $S$ . The horizontal line marked  $S_0$  at 0.477 represents the assumed mean value of the specific heat at zero pressure. The circle marked C represents the first experimental value 0.496 at 108° C. and 1 atmosphere; that marked B Brinkworth's more recent value 0.487 in terms of the mean caloric. Both of these give slightly lower values than 0.477 for the specific heat  $S_0$  at zero pressure. The circles marked R and III, indicate the observations of Regnault and of Holborn and Henning respectively at atmospheric pressure. The circles marked HS indicate the observations of Holborn and Henning reduced by assuming Swann's formula for air, which, as already explained, is probably too low at temperatures between 200° and 400° C.

**51. Knoblauch's Experiments.** The other points marked on the figure indicate the observations of Knoblauch and Jakob (*Forsch. Ver. Deut. Ing.*, 1906, 36, p. 109), at pressures of 2, 4, 6, and 8 kg./cm.<sup>2</sup>, and those of Knoblauch and H. Mollier (*loc. cit.*, 1911, 109, p. 79). The points belonging to the later series of observations are enclosed in circles, each of which represents the mean of several observations. They agree closely with the earlier series, being made by the same method with similar apparatus, except

that all the dots representing the observations at the lowest pressure of 2 kg./cm.<sup>2</sup>, are slightly higher in the later series than in the earlier between 150° and 200° C., but much lower in the later

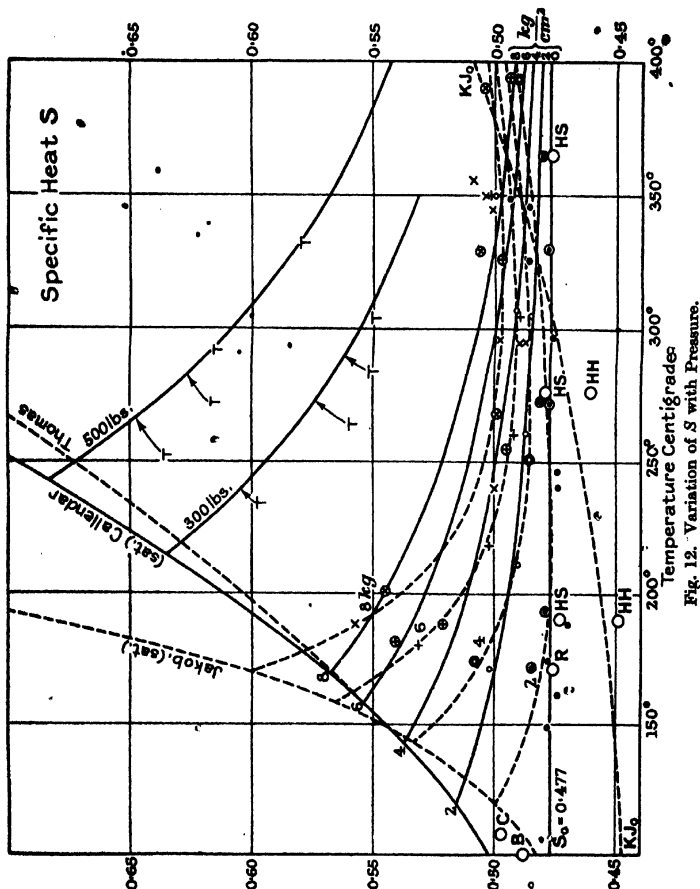


Fig. 12. Variation of  $S$  with Pressure.

series than in the earlier in the neighbourhood of 350° and above. The dotted curves marked 2, 4, 6, 8, represent the smoothed table of results given by Jakob (*Zeit. Ver. Deut. Ing.*, 1912, p. 1982) to fit both series of observations as closely as possible. The points at

different pressures are distinguished in the figure by the same marks as in the original papers, namely dots for the observations at 2 kg./cm.<sup>2</sup>, small circles for 4 kg., crosses (+) and (x) for 6 and 8 kg. respectively. The points at different pressures are well separated below 200° C., but begin to overlap at 300° C. and above, where the 4, 6, and 8 kg. points lie very close together. It will be seen that the observations confirm the variation of the specific heat with pressure, as predicted from the observations on the cooling-effect, not only in kind, but also in magnitude. The range of variation shown by the observations is in fact almost identical at 210° C., but somewhat greater below that temperature, and somewhat less above.

The dotted line marked  $KJ_0$  represents the extrapolated value of the specific heat at zero pressure given by Knoblauch and Jakob in their first paper. This showed a variation of  $S_0$  with temperature ranging from 0.447 at 100° C. to 0.509 at 400° C. which was supported by Holborn and Henning's\* original value 0.449 at 190° C. But the range of variation, amounting to nearly 14 per cent., appeared inadmissible in the light of subsequent reductions (*Brit. Assoc. Rep.*, 1908, p. 339). The observations of Knoblauch and Jakob in 1906, did not extend beyond 350°. The high values obtained at this point were inconsistent with the lower values subsequently obtained by Knoblauch and Mollier at higher temperatures. In Jakob's latest reduction, the upper end of the  $S_0$  curve has accordingly been lowered to 0.489 at 400° C., and the lower end raised to 0.461 at 100° C., reducing the variation to about 6 per cent., which is a more reasonable value. Knoblauch and Mollier reduce the variation still further, to about 4 per cent., as would seem to follow from their observations at a pressure of 2 kg. Since the points marked R and HS at 1 atmosphere should, if anything, be further raised, it appears probable that the 2 kg. points of Knoblauch and Mollier are still too low. This would require a similar adjustment of the 4 kg. curves, and would bring their results into better agreement with the author's.

**52. Values of  $S$  at Saturation.** It is difficult to measure the specific heat near saturation by direct experiment on account of the risk of water being carried with the steam, which would make the specific heat appear too high. Thus one per cent. of water in the steam would make  $S$  about 50 per cent. too high if measured over a range of 20° C. For the lowest observations in the Munich

experiments, the steam was first raised to a temperature about  $10^\circ$  or  $20^\circ \text{C}$ . above saturation in a superheater, from which it passed to the calorimeter, where the watts required to raise it another  $80^\circ$  or  $40^\circ \text{C}$ . were observed. In the first series, only two experiments gave values of  $S$  appreciably exceeding 0.50, namely 0.557 at 8 kg. and 0.531 at 6 kg., both points being exceptionally close to the saturation line. It is possible that these may have been affected a little by entrained moisture, since the observations between  $200^\circ$  and  $250^\circ \text{C}$ . are abnormally low in comparison. In any case it is obvious that the extrapolation of the curves to the saturation line must be of a very speculative character owing to the distance to be covered and the paucity of observations.

In the earlier paper, the curves of Knoblauch and Jakob appear to have been produced to the saturation line by purely graphic estimation. The points on the saturation line thus found at 2, 4, 6, and 8 kg., were connected by an empirical formula

$$S_s = 0.41 + 2.52 \times 10^8 / (T_c - T_s)^4, \dots\dots\dots(2)$$

where  $T_c$  is the critical temperature and  $T_s$  the saturation temperature at the point considered. With starting points given by this formula at saturation, a series of parallel curves were drawn showing values of  $S$  up to pressures of  $20 \text{ kg./cm.}^2$ ; but very little weight could be attached to a graphic extrapolation of this kind without any theoretical basis.

Jakob, in his later reduction (1911), employed a different empirical formula for the saturation values, namely,

$$S_s = 0.455 + 2 \times 10^{-20} T_s^8 / (T_c - T_s), \dots\dots\dots(8)$$

This is the formula represented by the dotted line marked Jakob (sat.) in Fig. 12. It gives a smaller range of variation than (2) at high temperatures, and raises all the saturation values by about 0.020 over the experimental range from 2 to  $8 \text{ kg./cm.}^2$ , which brings them into better agreement with the author's, but the formula has no theoretical foundation.

**53. Calculation of  $S - S_0$  from the Characteristic Equation.** The only satisfactory method of extrapolating experimental results for  $S$  to the saturation line is by the aid of some form of characteristic equation which is known to represent the other properties of steam in the neighbourhood of saturation. The variation of  $S$  with pressure at constant temperature for any

substance is given by the well known differential equation (Appendix I (48))

$$(dS/dP)_t = -aT(d^2V/dT^2)_P, \dots\dots\dots(4)$$

which is easily solved if  $V$  is known as a function of  $T$  and  $P$ . The Author's equation gives in this way the general expression for  $S$ ,

$$S = S_0 + an(n+1)cP/T, \dots\dots\dots(5)$$

where  $n = 10/3$ ,  $a = 10,000/427$  (K.M.C.), and  $c = 0.0263 (373/T)^3$  (K.M.C.). A similar result is easily obtained from Linde's equation,

$$S = S_0 + an(n+1)cP(1+0.01P)/T, \dots\dots\dots(6)$$

where  $a = 10,000/427$  (K.M.C.),  $n = 3$ , and  $c = 0.031 (373/T)^3$ . This expression is exactly similar to the author's, but with different values of  $c$  and  $n$ , and with the addition of the small correction term  $0.01P$  depending on  $P$ , which makes it give higher results at high pressures.

The corresponding expressions for the product  $SC$  are

$$\text{Author } SC = a(n+1)c - ab, \dots\dots\dots(7)$$

$$\text{Linde, } SC = a(n+1)c(1+0.02P) - 0.0052a, \dots\dots\dots(8)$$

The constants have the values given above on the (K.M.C.) system. It will be seen that the correction term  $0.02P$  in expression (8) for  $SC$  is twice as great as in the corresponding expression for  $S$ .

The following table shows a comparison of Jakob's extrapolated values with the variation of  $S$  at saturation deduced from the two equations.

Table II. Values of  $S$  at Saturation.

Pressure kg./cm. <sup>2</sup>	Author 1902	Linde 1905	Thomas 1907	Knoblauch and Jakob	Jakob 1911
0	0.461	0.461	0.461	0.447	0.461
2	0.499	0.500	0.500	0.480	0.499
4	0.522	0.525	0.524	0.513	0.533
6	0.539	0.545	0.540	0.548	0.566
8	0.554	0.565	0.552	0.583	0.600

Jakob's values have been taken from his 1911 paper without modification, but the others have been reduced to Jakob's later values of  $S_0$  (which range from 0.461 at 2 kg. to 0.463 at 8 kg.) for purposes of comparison, since the characteristic equations do not give  $S_0$  but only  $S - S_0$ . The extrapolated values assumed for

$S_0$  at 100° C. and zero pressure, are given in the first line. They are taken as 0.461, except for Knoblauch and Jakob, where the curve ( $KJ_0$ ) gives the value 0.447. It will be seen that both the characteristic equations give differences of  $S$  diminishing with rise of pressure; whereas the Knoblauch and Jakob columns show nearly equal differences, which is the natural tendency of all graphic methods in which the proper run of the curves is estimated by eye. Thus, according to the author's equation the successive differences of  $S$  are 38, 23, 17, 15, diminishing with rise of temperature; but according to Knoblauch and Jakob, 33, 33, 35, 35, and according to Jakob (1911), 38, 34, 33, 34. Linde's equation shows a range of variation of 0.065 from 2 to 8 kg. which is somewhat greater than the author's 0.055, but much less than Jakob's 0.101. In an extrapolation of this kind it is reasonable to attach greater weight to values deduced from an equation which is known to represent the volume correctly, than to a graphic or empirical method, because the variation of  $S$  with pressure depends directly on the variation of the volume. If the starting points selected by Jakob at 2, 4, 6, 8 kg. on the saturation curve are so uncertain, the uncertainty of the empirical extrapolation to 20 kg. is many times greater.

**54. Experiments of Thomas.** The experiments of Thomas (*Trans. Amer. Soc. Mech. Eng.*, 29, pp. 1021-1067, 1907) are of special interest and importance in this connection because he used the saturation limit itself as the starting point of his measurements, and directly observed the watts required (1) to dry a given current of steam, and (2) to superheat it through ranges of 10°, 20°, 40°, 60°, 80°, 100°, and 150° C. The pressure was varied from 7 to 500 lbs./sq. in., and special attention was devoted to measuring and eliminating the heat-loss. By surrounding the calorimeter with an electrically heated and highly polished jacket, he was able to reduce the external loss practically to zero, but he also tried other methods in which the conditions as to heat-loss were widely varied. His calorimeter had a very small thermal capacity as compared with the massive oil-bath of Knoblauch and Jakob. This is quite an important point in a steady-flow method. The temperatures were taken with thermo-couples, and the watts with a direct reading instrument, which precluded a high order of accuracy in the observation of small differences, but was well suited for the measurement of the total heat. The watts required to dry the steam were obtained by observing the point at which

the temperature first began to rise above that of saturation when the watts were increased. It would appear from Thomas's observations that the water present in the original steam supply often amounted to 3 or 4 per cent. Owing to the time taken to evaporate small drops of water in a rapid current of steam when the superheat is very small, it is practically certain that a small proportion of water was still present in the steam when the temperature first began to rise above the saturation point. It appears in fact from an analysis of the observations that the proportion of water present at this stage was nearly the same in all cases, and amounted to about one-fifth of 1 per cent., being equivalent to nearly 1 calorie C. This would raise all the values of the specific heat obtained over the first interval near saturation by an equal amount, but would not materially affect the accuracy of the results for the *variation* of the specific heat along the saturation curve.

It is noteworthy that if Thomas's curve for  $S$  at saturation is reduced to the same value as the author's at 2 kg., it practically coincides with the author's from 2 to 8 kg., so that it could not be shown separately on the scale of the figure. Beyond this point it begins to diverge slightly from the author's, lying a little *below* it as indicated by the broken line marked Thomas. But the deviation appears to be within the limits of possible error in such difficult experiments, considering the small number of points actually obtained at the higher pressures. No doubt it is true that the author's theoretical results at saturation appear excessively low as compared with Jakob's extrapolated values. But they err a little in the opposite direction when compared with Thomas's experimental values, and there should be little hesitation in such a case in giving greater weight to the results of actual experiments at high pressures than to a purely speculative extrapolation.

Thomas's observations at 300 and 500 lbs. are shown in Fig. 12 by the marks T in relation to the author's theoretical curves at these pressures. The two highest values of the specific heat actually observed by Thomas, as given in his tables, at a pressure of 500 lbs./sq. in., were 0.686 between 242° C. (sat.), and 262° C., and 0.617 between 262° and 282° C. The author's formula gives 0.668 and 0.689 respectively over these ranges, which show reasonably good agreement considering that it was difficult to keep the quality of the steam quite constant at this high pressure. Thomas's points at 292° and 332° fall exactly on the author's curve at 500 lbs. Linde's formula, taking  $S_0 = 0.461$  (Jakob), gives 0.744 and 0.704 for the



first two points, values which appear to be too high owing to the correction term  $(1 + 0.01P)$ , which raises the value of  $S$  by about 0.100. On the other hand, Jakob's first formula for  $S$  at saturation gives  $S = 1.511$  at  $242^\circ \text{C.}$ , and his second formula gives  $S = 1.260$ . The highest value actually observed by Knoblauch and Jakob was only 0.557. It appears inconceivable, in the light of Thomas's experiments, that the specific heat at 500 lbs. could possibly be as high as 1.260, even at saturation, where the author's formula gives 0.684, or a linear extrapolation of Thomas's values 0.646.

**55. Variation of  $S$  with Pressure at  $260^\circ \text{C.}$**  The actual observations of Knoblauch and Jakob, and Knoblauch and Mollier agree very well with Linde's equation for the variation of  $S$  in the neighbourhood of  $200^\circ \text{C.}$ , where the observations at different pressures are well separated. They agree equally well with the author's equation at  $210^\circ \text{C.}$  But at higher temperatures the observations at different pressures begin to overlap, owing to experimental errors, and the pressure variation of  $S$  cannot be determined with any certainty from the observations themselves, because the variation is of the same order as the experimental errors. The smoothed curves and tables given by Jakob appear to make the variation a little too small as compared with the characteristic equation, or with Thomas's experiments. This is shown by the following table of values at  $260^\circ \text{C.}$

• Table III.

Values of  $S - S_0$  at  $260^\circ \text{C.}$ , from 2 to 16 kg./sq. cm.

Pressure kg./cm. <sup>2</sup>	2	4	6	8	10	12	14	16
Jakob, table	0.007	0.015	0.023	0.032	0.042	0.052	0.062	0.074
Thomas, curves	0.011	0.021	0.032	0.043	0.053	0.063	0.073	0.081
Author, calc.	0.0102	0.0204	0.0305	0.0407	0.0509	0.0611	0.0713	0.0814
Linde, calc.	0.0114	0.0233	0.0356	0.0484	0.0616	0.0753	0.0894	0.1046

There is strong theoretical evidence that the lines should be equally spaced for moderate pressures at any given temperature. The equal spacing of Knoblauch and Jakob's curves (1907) at low pressures was reduced by Jakob (1911) on account of the raising of the 2 kg. curve in the later experiments by Knoblauch and Mollier. Otherwise they agree very well with the author's difference of 0.0102 for 2 kg. at moderate pressures, but show a

more rapid increase with pressure as saturation is approached at constant temperature. Thomas's curves on the other hand, show practically the same spacing as the author's up to 16 kg. but a smaller rate of increase with pressure at higher pressures. The difference is of no great practical importance, and the experimental evidence does not appear to justify the adoption of a more complicated formula than the author's. Linde's equation gives somewhat larger differences increasing with pressure, and does not seem to agree so well with observation over the experimental range.

**56. Rate of Variation of  $H$  with  $T$  for Saturated Steam.** The variation of  $H$  with temperature for saturated steam can be deduced from the values of  $S$  and  $C$  at saturation by the general formula (7) of Chapter III (see also Appendix I (15)),

$$(dH/dT)_s = S - SC (dp/dT)_s \dots\dots\dots(9)$$

But as neither  $S$  nor  $C$  can actually be measured at saturation, the most appropriate use of this formula is to deduce the values of  $(dH/dT)_s$  corresponding to any particular type of characteristic equation assumed. The characteristic equation gives  $S - S_0$  and  $SC$  directly, and the value of  $(dH/dT)_s$  is then made to depend on those of  $S_0$  and  $dp/dt$  which are known with a fair degree of certainty. Similarly if  $(dH/dT)_s$  were given, the formula might be employed to deduce consistent values of  $C$  from those of  $S$ , or *vice versa*. If thermodynamically consistent formulae are employed for *all* the properties, such tests are superfluous, because all such calculations must lead to identical results; but if empirical formulae derived from experiment are employed, the equation affords a useful and necessary test of consistency.

The following table shows a comparison of values of  $(dH/dT)_s$  obtained by different methods. The first column gives the values taken from Henning's table of  $H$ , or  $L$  (Chapter II), which showed such remarkable agreement with those previously calculated by Linde from his characteristic equation by the aid of Clapeyron's formula. The corresponding values of Linde are given in the second column headed Linde-Clapeyron. The values in the third column, headed Linde,  $S$  and  $C$ , have been calculated by (9) from Linde's equation using his own values of  $dp/dt$ , and choosing  $S_0$  to give the same change of  $H$  as the previous column between  $100^\circ$  and  $180^\circ$ . Values deduced in this way are likely to be more correct in the neighbourhood of  $100^\circ$  C. than those deduced from Clapeyron's

relation, which throws too much weight on possible errors of  $dp/dt$ . They also show a diminution with rise of temperature, as required by theory, instead of tending to a constant value 0.81 as in Henning's table. But the diminution shown is much too rapid near 200° C., and would make  $H$  reach a maximum in the neighbourhood of 210° C. for saturated steam, which is most improbable, and tends to show that the correction term  $0.02P$  in Linde's equation is erroneous.

Table IV.

Values of  $dH/dT$  for Saturated Steam by different formulae.

Temp. Cent.	Henning, Table	Linde, Clapeyron	Linde, $S$ and $C$	Davis, Parabola	Davis, $S$ and $C$	Davis-Thiesen		Author's equation
						$t, 365$	$t, 374$	
100°	0.36	0.34	0.398	0.374	—	0.367	0.388	0.404
120°	0.32	0.34	0.361	0.335	0.331	0.340	0.363	0.373
140°	0.31	0.31	0.343	0.295	0.306	0.309	0.334	0.337
160°	0.31	0.31	0.252	0.256	0.280	0.275	0.305	0.299
180°	0.32	0.31	0.177	0.216	0.250	0.237	0.272	0.259
200°	—	—	0.080	0.176	0.209	0.192	0.233	0.222

The values in the column headed Davis, parabola, are calculated from the parabolic formula of Davis (*Trans. Amer. Soc. Mech. Eng.*, xxx, p. 741, 1909) which gives

$$(dH/dT)_s = 0.3745 - 0.00198(t - 100). \dots\dots(10)$$

This is a purely empirical formula calculated from the throttling experiments of Grindley, Griessmann and Peake, and is not suitable for extrapolation below 100° C. because it deviates widely from experiment in this region, and would make  $S = 0.578$  at 0° C. Between 120° and 180° C. the formula represents the observations on which it was founded satisfactorily, but it appears probable that the experiments themselves were affected by systematic errors due to heat-loss, which tend to make the rate of increase of  $H$  too small. It is obvious that a linear formula for  $(dH/dT)_s$  (corresponding with a parabola for  $H_s$ ) cannot easily be reconciled with other properties of steam, or with any reasonable form of characteristic equation, such as that of Linde, which Davis adopts for the volume. It is also inconsistent with the values of  $(dH/dT)_s$  calculated by formula (9) from the values selected by Davis for  $S$  and  $C$ , as shown in the next column. Davis in a later paper (*Proc. Amer. Acad.*, xlv, p. 284, 1910), recommends a formula of the Thiesen type (see Chapter II) for extrapolation, which gives the values of  $(dH/dT)_s$

in the column headed  $t_c$  365°. The agreement of this formula with observations below 100° C. is greatly improved if the correct value,  $t_c = 374^\circ$ , is substituted for the critical temperature, which is the chief justification for the employment of the formula for extrapolation. The effect of this correction is to raise the values of  $H$  by about 3 calories in the neighbourhood of 200°, where they are brought into exact agreement with the author's equation for  $H$ .

It will be observed that Davis's parabolic formula would make  $H$ , a maximum, or  $(dH/dT)_c = 0$ , when  $t = 289^\circ \text{C.}$ , whereas the Davis-Thiesen formula with  $t_c = 365^\circ$  would make  $H$  a maximum at  $t = 259^\circ \text{C.}$ , and with  $t_c = 374^\circ$  would give a maximum for  $H$  at  $t = 277^\circ \text{C.}$  In the discussion on Davis's paper, Prof. Marks (*loc. cit.*, p. 765) gave it as his opinion that "the true curve should lie somewhat higher at high pressures than the Davis curve, and that an equation giving a maximum value of the total heat at a temperature considerably nearer the critical point would represent the facts better than the equation proposed." Without laying too much stress on the position of the maximum, which is a somewhat speculative question, one may at least assert that an equation of the Thiesen type, with  $t_c = 374^\circ$ , which gives the correct result for  $L$  at the critical temperature, and a maximum at a lower point than Davis's curve, is not likely to give results which are much too high in the neighbourhood of 200° C. Moreover it gives very fair agreement with experiment even at temperatures below 100° C., and also agrees with Henning's observations at 180° C., which are most likely to err, if anything, in defect, like all other observations on the latent heat. On the other hand the Davis parabola gives a value 3 calories C. lower than Henning's experiments at 180° C., and lower than some of Regnault's observations at 190° C., which are likely to be at least 3 calories too low, since it is very improbable that he could have succeeded in eliminating the wet-steam error more completely at 190° than at 100° C. On these grounds it would appear probable that the author's theoretical formula, deduced from throttling experiments by the differential method, may be more nearly correct than the Davis formula in the neighbourhood of 200° C., as it gives much better agreement with observation below 100° C., and is also in practically perfect agreement with the Thiesen formula at temperatures up to 240° C.

**57. Calculation of  $S$ , at Saturation from  $(dH/dT)$ , or  $dL/dT$ .** In consequence of the difficulty of measuring  $S$  near

saturation, many attempts have been made to calculate appropriate values from various formulae assumed for  $(dH/dT)_s$ , by means of the general relation (9) given in the preceding section. In order to do this it has been usual to substitute for  $SC$  from the relation

$$SC = aT (dV/dT)_s - aV, \dots\dots\dots (11)$$

and for  $dp/dt$  from Clapeyron's equation, which gives the expression for  $S$ ,

$$S = (dH/dT)_s + L (dV/dT)_s / (V - v) - LV/T (V - v), \dots (12)$$

but these substitutions are purely a matter of form if it is understood that  $SC$  is calculated from some form of characteristic equation for  $V$ , and that the values of  $V$  satisfy Clapeyron's equation, as is generally the case.

If a formula for  $L$  is given in place of  $H$ , the value of  $(dH/dT)_s$  is taken as  $dL/dT + dh/dT$ . The formula in this shape was given by Planck (*Thermodynamics*, Eng. Trans. 1903, p. 147) as a "rigorous, test of the second law" of thermodynamics, and is often known as "Planck's formula." He obtained the formula in a different way, and made the additional substitution

$$s = (aT (dv/dt)_p - av) (dp/dt)$$

for  $dh/dt$ . But this is undesirable, because  $dh/dt$  is the quantity most easily measured for the liquid at temperatures above 100° C. It is simpler to keep the formula in the shape (9), as being the direct expression of the relation between  $S_s$  and  $(dH/dT)_s$ , because the effect of different assumptions is then immediately obvious.

The formula has already been applied (Table III of Chapter IV) as in (*R. S.*, 1900), to determine the variation of  $S_s$  when given values are assumed for  $SC$  and  $(dH/dT)_s$ . It is not so well adapted to give  $S_s$  in terms of  $(dH/dT)_s$  if  $C_s$  is given, because a small error in  $C$  or  $dH/dT$  involves a relatively large error in  $S$  at high temperatures when  $Cdp/dt$  is nearly equal to 1, and because the value of  $S$  becomes indeterminate, or infinite, when  $Cdp/dt$  reaches unity.

Thiesen (*Ann. Phys.*, 9, p. 80, 1902) employed a formula of this type to calculate  $S_s$  for steam, assuming his original formula for  $L$ , with the index  $\frac{1}{3}$ , and 365° C. for the critical temperature. He took the expression  $K/T^3$  for  $SC$  from the original Joule-Thomson equation, and calculated  $K$  from Clapeyron's equation at 100° C. He thus found values of  $S$  at saturation ranging from 0.486 at 0° C., to a minimum 0.415 at 80° C., and rising again to 0.51 at

180° C. There is no experimental evidence for such a minimum, but the method gives more reasonable results if Thiesen's original formula is corrected to agree with observed values of the latent heat as previously explained, provided that a suitable type of characteristic equation is used. Having found values of  $S_s$  by this method, Thiesen proceeded to deduce consistent values of  $S_0$  from the expression for  $S - S_0$  given by the characteristic equation assumed for SC. This is evidently an essential part of the process, because the values of  $S_s$  deduced by this method cannot be harmonised with any arbitrary values of  $S_0$  determined by experiment or selected by an independent method.

### 58. Erroneous Application of Planck's Equation.

Davis (*Trans. Amer. Soc. Mech. Eng.*, xxx, p. 750, 1909) employed the same method in order to corroborate the high values given by Knoblauch and Jakob (Münich) at saturation. He quotes Planck's formula in the shape (12) given above, except that he neglected  $v$  in the last term, which then reduces to  $L/T$ . The effect of this is to increase the value of  $S$  by 0.010 at 200° C. He assumed  $dH/dT$  and  $L/T$  from his own parabolic formula for  $H_s$ ;  $(dV/dT)_s$  from Linde's equation, and  $L/(V - v)$  from Henning's values of  $dp/dt$ . Since Linde's values of  $V$  satisfy Clapeyron's equation with Henning's values of  $L$  and  $dp/dt$ , the result is practically the same (except for the neglect of  $v$ ) as if the last two terms in Davis's equation (12) were replaced by  $SCdp/dt$ . The results found in this way agreed with Knoblauch and Jakob's extrapolation in giving the exceptionally high value,  $S_s = 0.795$  at 205° C., and were generally regarded at the time (in America) as a conclusive confirmation of the Munich extrapolation. The comparison was repeated by Davis in a later paper (*Proc. Amer. Acad.*, xlv, p. 297, 1910) and made more convincing by showing that Thomas's values of  $H$  led to slightly higher results for  $S$  than the parabolic formula for  $H$ . The reason of this is that Thomas's values of  $(dH/dT)_s$ , as reduced by Davis, are slightly higher than the values given by Davis's formula for  $H_s$ , and agree more nearly with the author's. The author's values of  $(dH/dT)_s$ , if added to Linde's values of  $SCdp/dt$ , would give still higher values of  $S_s$ .

Davis does not appear to have made any experiments himself in support of his formula, but his conclusions were accepted in America without serious criticism "as the most valuable contribution to the science and practice of steam-engineering since the

determination of the mechanical equivalent of heat by Rowland." The parabolæ formula for  $H$ , in spite of its obvious defects, was accepted by Peabody as the basis of his new tables, and Jakob revised his extrapolation of  $S$  at saturation to conform as closely as possible with the values calculated by Davis from "Planck's" equation (12).

Davis's calculation of  $S_s$  from "Planck's equation" (12) was very effective at the time in discrediting the experiments of Thomas and supporting the empirical extrapolation of Knoblauch and Jakob; but it rests on a fundamental fallacy, and cannot be seriously maintained. The thermodynamical equation (9) is no doubt exact, but it merely gives the values of  $S$  at saturation which are required to harmonise the Davis formula for  $H$  with Linde's values of  $SC$  at the saturation point, and leads to excessive discrepancies at all other points. The method fixes the values of  $S$  along the saturation line by an arbitrary conjunction of two inconsistent formulæ which cannot be reconciled on any reasonable hypothesis. The effect of this is most easily seen by calculating the values of  $S_0$  at zero pressure from Linde's equation corresponding to those of  $S$  at saturation given in the table calculated by Davis. The values are collected for comparison in the following table.

Table V.  
Comparison of Davis's values of  $S_s$  with Jakob and Linde.

Temp. Cent.	Values of $S$ at saturation				Values of $S_0$		$(dH/dT)$	
	Knoblauch and Jakob	Davis- Planck	Jakob 1911	Linde- Jakob	Davis- Linde	Jakob 1911	Davis parabola	Linde- Jakob
100.6°	0.470	0.484	0.484	0.486	0.469	0.461	0.378	0.375
126.3°	0.492	0.506	0.509	0.504	0.463	0.461	0.322	0.320
153.1°	0.537	0.560	0.558	0.538	0.484	0.462	0.270	0.248
170.1°	0.584	0.615	0.608	0.565	0.513	0.463	0.236	0.186
193.2°	0.699	0.722	0.715	0.613	0.573	0.464	0.190	0.081
205.1°	0.795	0.794	0.796	0.644	0.615	0.465	0.166	0.016
215.8°	0.919	0.875	0.892	0.676	0.665	0.466	0.145	- 0.054
225.1°	1.068	0.956	0.997	0.708	0.715	0.467	0.127	- 0.121
235.8°	1.318	1.067	1.150	0.749	0.786	0.468	0.106	- 0.212
245.2°	1.634	1.179	1.323	0.790	0.858	0.469	0.087	- 0.302
253.5°	2.041	1.293	1.514	0.830	0.933	0.470	0.071	- 0.392

The first empirical formula (No. (2) p. 104) of Knoblauch and Jakob (1907) gave the values of  $S_s$  quoted by Davis and shown in the first column. These did not agree very well with those calculated by Davis from Planck's equation and given in the second column,

except that the curves intersected at  $205^{\circ}\text{C.}$ , and were of a similar type; but Jakob in his second empirical formula (1911), quoted as No. (8) in this chapter, succeeded in bringing his results into very fair agreement with those calculated by Davis over the experimental range. The values of  $S_s$  in the fourth column are calculated from Linde's equation for  $S - S_0$  by employing Jakob's latest values of  $S_0$  (1911) given in the sixth column. They are seen to be quite inconsistent with the values calculated by Davis, showing less than half the range of variation. The same result is shown in the next column by calculating the variation of  $S_0$  with temperature required by the Davis values of  $S$  at saturation. These show that if the Davis formula and Linde's equation are both assumed to be correct at saturation, the value of  $S_0$  must increase rapidly with temperature, reaching a value  $0.933$  at  $253.5^{\circ}\text{C.}$ , nearly double that given by Jakob.

The values of  $(dH/dT)_s$ , calculated from Linde's equation by assuming Jakob's values of  $S_0$ , are shown in the last column, for comparison with those given by the Davis parabola. The Linde values give a maximum for  $H_s$  at  $207.5^{\circ}\text{C.}$ , and a high negative value of  $(dH/dt)_s$  at  $253.5^{\circ}\text{C.}$ , which is obviously impossible. The reason is simply that the values of the term  $SCdp/dt$  given by Linde's equation are far too large, owing to the  $P$  correction factor  $(1 + 0.02P)$ , which reaches the value  $1.86$  at  $253.5^{\circ}\text{C.}$ , and represents chiefly errors of reduction and surface-condensation in the Munich experiments on  $V$ . The high values of  $S_s$  obtained by Davis from Planck's relation are due almost entirely to Linde's  $SCdp/dt$ , which reaches the value  $1.222$  at  $253.5^{\circ}\text{C.}$

But if the values of  $SC$  given by Linde's equation are much too high, it follows that those of  $S - S_0$  must also be too large, since they depend on the same constants, and one cannot be reduced without reducing the other. If the values of  $SC$  are reduced in comparison with those of  $S - S_0$ , so as to obtain reasonably good agreement with values of  $(dH/dT)_s$  given by experiment, we find that the variation of  $S_s$ , shown in the fourth column under the heading Linde-Jakob, which is already less than half that given by the Davis-Planck calculation, is thereby further reduced to give very fair agreement with the variation shown by the author's equation or by Thomas's experiments.

It might conceivably be argued that it is justifiable to use Linde's values of  $SC$  or  $(dV/dT)_s$  in the neighbourhood of saturation, without assuming that his equation applies at other points.



But it is just at this point that the errors of his formula, as shown by the variation of  $H_s$ , are most conspicuous. It would of course be absurd to calculate  $H$  or  $\Phi$  with values of  $S$  taken from Linde's equation with the Davis-Planck values at saturation; but even if Linde's equation is used only for the volume and Jakob's values exclusively for  $S$ , the two assumptions, being thermodynamically inconsistent, will inevitably give rise to material discrepancies.\* (See Appendix I, § 180.)

**59. Calculation of  $S$  from  $C$ .** One of the most appropriate uses of the observations on the cooling-effect  $C$ , is for deducing the variation of  $S$  with pressure, as already explained, from the expression for  $S - S_0$  given by the characteristic equation. Since the variation  $S - S_0$  is generally a small part of the whole specific heat, there is little chance of serious error in this method even if  $c$  is not very accurately known. Thus to take an extreme case, an error of 4 per cent. in  $c$  at  $200^\circ \text{C}$ . would produce an error of only 1 per cent. in  $S$  at saturation pressure, and a much less error at lower pressures.

If on the other hand we attempt to calculate  $S_s$  from equation (9) or (12) in the form

$$S_s = (dH/dT)_s / (1 - C dp/dt),$$

by assuming a formula for  $H$  or  $L$ , and employing experimental values of  $C$ , any error in  $C$  is multiplied many times at temperatures above  $200^\circ \text{C}$ ., when  $C dp/dt$  approaches unity. Thus if we take  $(dH/dT)_s = 0.1755$  from Davis's formula at  $200^\circ \text{C}$ ., and

$$C = 0.155^\circ \text{C./lb.}$$

from Davis's curve, we find  $S_s = 0.650$ , which agrees fairly with the Linde-Jakob column in Table V, but is much smaller than the value 0.744 given by interpolation in the column headed Davis-Planck. Davis does not give results obtained by this method, though it might easily be employed to support Jakob's extrapolation. If we wished to get the value 0.744 for  $S_s$  at  $200^\circ \text{C}$ . with

$$(dH/dT)_s = 0.1755,$$

it would suffice to take  $C = 0.162$ , which is within the limits of uncertainty of the experiments on which Davis's curve for  $C$  is founded. But if we take  $C_s = 0.192^\circ \text{C./lb.}$ , the value given by Linde's equation, we find  $S_s = 1.81$  at  $200^\circ$ , which is absurd. It would obviously be inconsistent to use Davis's value of  $(dH/dT)_s$  in place of Linde's in such a case, though this is precisely what Davis did in applying Planck's relation. Linde's equation gives

values of  $C$  at  $200^{\circ} \text{C.}$  increasing from  $0.151^{\circ} \text{C./lb.}$  at zero pressure to  $0.192$  at saturation pressure, instead of diminishing with increase of pressure, and the values at high pressures appear to be irreconcilable with experiment.

Jakob, in his later reduction (1911), beyond stating that the values for  $S$ , calculated by Davis from Planck's relation show a remarkable coincidence with his later empirical formula (which is not to be wondered at), makes no use of Linde's equation to support his own values of  $S$  at other points, since it would evidently be impossible to secure any reasonable agreement.

**Special Case,  $C = F(T)$ .** The relation between the specific heat and the cooling-effect takes a simple form, as already explained in Chapter IV, when  $C$  is a function of the temperature only. The equation of a line of constant  $H$  on the  $PT$  diagram is immediately obtained in analytical form by integrating,  $dP = dT/C$ , if  $1/C$  is any integrable function of  $T$ . The integral may be put in the form  $P + P_0 = F(T)$ , where  $P_0$  is the constant of integration. This one solution includes *all* the lines of constant total heat, since they must all have the same slope at the same temperature. The value of  $P_0$ , corresponding to any particular line which may be required, is obtained by substituting the values of  $P$  and  $T$  for any given point on the line.

If  $C$  is not given as a function of  $T$  explicitly, but merely as an arbitrary curve derived from experiment, the solution is readily obtained in the form of a table of corresponding values of  $P + P_0$ , or  $F(T)$ , and  $T$ , by the arithmetic process of summing values of  $1/C$  tabulated for each degree of temperature. The part of the table corresponding to any particular line, extending from  $P = 0$  to  $P = p$  at saturation temperature  $t_s$ , is easily found by taking the value of  $P + P_0$  from the table at  $t_s$ , and subtracting  $p$ , which gives  $P_0$  for the particular line required. The coordinates  $P$  and  $T$  of any point on the line will serve equally to determine  $P_0$  for that line.

To find the value of  $S$  at any point of a line of constant  $H$ , in terms of the value  $S_0$  at any standard pressure, such as  $P = 0$ , or  $P = 1$  atmosphere, on the same line we have the result, already proved (equation (7) of Chapter IV), that  $SC$  is constant along a line of constant  $H$ , if  $C$  is a function of  $T$  only. In other words we have  $S/S_0 = C_0/C$ , where  $C_0$  is the value of  $C$  at the given standard pressure on the same line, which is known from the table of  $C$  and  $T$ , and  $P + P_0$ .

If an expression for  $C$  as a function of  $T$  is given, the expression for  $S$  may be put in the corresponding analytical form by the method previously explained in Chapter IV. Thus, if  $C = K/T^n$ , we obtain, from (11) of Chapter IV,

$$S/S_0 = C_0/C = (T/T_0)^n = (1 - (n+1)CP/T)^{-n/(n+1)}, \dots (18) \bullet$$

where  $S_0$  is the value of  $S$  when  $P = 0$ , on the line of constant  $H$ , through the point  $PT$ .

• The method is mathematically complete, but is liable in practice to two objections for calculating  $S$ . (1) Any error in  $C$  gives an equal proportionate error in  $S$ , instead of affecting the *variation* of  $S$  only. (2) The assumption that  $C$  is a function of  $T$  only, is not necessarily true, and may introduce additional errors in  $S$ .

Davis (*Proc. Amer. Acad. Sci.*, 45, p. 291, 1910) devised an ingenious method based on the general relation

$$(dS/dP)_H = -S(dC/dT)_p, \dots (14)$$

which may also be written in the form\*

$$\log_e (S/S_0) = - \int_{P_0}^P (dC/dT)_p dP \quad (H \text{ constant}), \dots (15)$$

where the integration is to be performed along a line of constant  $H$ , and the ratio  $S/S_0$  refers to any two points on the same line at pressures  $P$  and  $P_0$ . The method of applying this formula is described by Davis as follows:

"The use of the new equation at ordinary temperatures is a matter requiring patience and much labour. First one computes and plots against  $t$  the derivative of the  $C = f(t)$  curve. Next one computes from the curve of  $C$  itself the progress of some line of constant  $H$  across the  $pt$  plane; this is necessary in order to be able to express  $dC/dT$  as a function of  $p$  in the integral. Then the integral has to be evaluated, either by replotting  $dC/dT$  against  $p$  for the particular  $H$  curve in question and using an integrator, or by a step by step numerical process. The results are the Napierian logs of the desired ratios."

Davis worked out the ratios in this way along four lines of

\* Davis leaves the equation in the exponential form,  $S/S_0 = e^{-x}$ , where  $x$  represents the integral. Jakob also quotes it in this form. But if  $C$  is a function of  $t$  only, as assumed by Davis, it is easy to see that  $(dC/dT)_p dp$  at constant  $H$ , becomes  $dC(dp/dt)_H$ , or  $dC/C$ , the integral of which between limits, taken with the negative sign, is simply  $\log_e (C_0/C)$ , giving the solution  $S/S_0 = C_0/C$ , already proved in a different way. Since it is unnecessary to make any use of the "derivative of the inaccurately known function  $C$ ," namely  $(dC/dT)_p$ , the objection urged by Davis against his own method does not apply to the author's.

constant  $H$  (1) from  $121^\circ$  to  $187^\circ$  C., (2) from  $149^\circ$  to  $180^\circ$  C., (3) from  $205^\circ$  to  $253^\circ$  C., and (4) from  $288^\circ$  to  $319^\circ$  C. Curve (1) did not agree at all with Knoblauch and Jakob's results. Curve (2) gave fair agreement only at  $180^\circ$  C. near saturation. Curves (3) and (4) gave fair agreement at high superheats; but the data for  $C$  in this region were based chiefly on the law of corresponding states, which introduces an additional element of uncertainty. Jakob made some use of the points on (3) and (4) in extrapolating his curves to 20 kg., which otherwise were devoid of any theoretical basis.

Davis also made some approximate calculations at  $485^\circ$ ,  $600^\circ$ ,  $925^\circ$ , and  $1480^\circ$  C. taking  $dC/dT$  and  $T$  constant at constant  $H$ , and assuming the law of corresponding states. The variation of  $S$  found at  $485^\circ$  C. was only about half that given by Knoblauch and Mollier's experiments, and was not accepted by Jakob.

The weakest point of the method, as explained by Davis, is "that 'the formula has the disadvantage of involving the derivative of the inaccurately known function  $C$ , which prohibits its use at low temperatures where  $C$  itself is scarcely known at all.'" But there is no reason why the method should not give fairly reliable values over the experimental range if the values of  $C$  employed for deducing  $H$  are correct. Unfortunately Davis gives only three lines of constant  $H$  between  $121^\circ$  and  $253^\circ$  C., which do not extend to saturation, or overlap, so that his solution is very incomplete. It is easy however to complete the solution by the author's method. The values of  $1/C$  taken from Davis's curve give by simple summation a table of corresponding values of  $P + P_0$  and  $t$ , which includes *all* the lines of constant  $H$ , and gives ratios of  $S/S_0 = C_0/C$  at *any* desired points.

The following table shows values of  $S$  at saturation calculated in this way from Davis's curve for  $C$ , for comparison with the empirical formulæ of Knoblauch and Jakob.

Table VI.  
Values of  $S$  at Saturation from Davis's Curve for  $C$ .

$P$ , kg./cm. <sup>2</sup>	2	4	6	8	10	16	20	26	31.7	37.3	42.9
$t$ , °C.	119.6	142.9	158.1	169.6	179.1	200.5	211.4	225.1	235.8	245.2	253.5
$S$ , Davis	0.543	0.576	0.600	0.621	0.640	0.690	0.730	0.792	0.838	0.885	0.933
$S$ , K. and J.	0.490	0.513	0.548	0.583	0.621	0.751	0.865	1.068	1.318	1.634	2.041
$S$ , Jakob	0.499	0.533	0.566	0.600	0.637	0.749	0.834	0.997	1.150	1.323	1.614

The values in the line  $S$ , Davis, are obtained from the ratios  $S/S_0$  by assuming Jakob's values of  $S_0$ , which range from 0.461 to 0.468 at the required zero points on the lines of constant  $H$ , and cannot introduce any material uncertainty. The difference  $S - S_0$  at 2 kg., deduced from the Davis curve for  $C$ , is more than twice as great as that assumed by Jakob, or given by Linde's formula. The reason is that Davis's curve for  $C$  (Fig. 10) runs much too high at 120° C., as already remarked, and gives values of  $dC/dT$  about twice as great as Grindley's curve, or as the differential method. The curve for  $S$  at saturation deduced from Davis's curve for  $C$  intersects the Jakob curve for  $S$ , in Fig. 12 near 10 kg., which is the only Davis point plotted by Jakob near saturation. On the other hand the difference  $S - S_0$  given by Davis's curve at 250° C. is much less than half that given by Jakob's extrapolation, or less than a third of that given by Knoblauch and Jakob's original formula. This is further proof, from Davis's own curve, that Jakob's empirical extrapolation gives impossible results.

**60. Comparison of Values of  $H$  deduced from  $S$ .** It has been necessary to discuss the speculations of Jakob and Davis with regard to the values of  $S$  at saturation in considerable detail, because so much use has been made of these and similar arguments to the discredit of the author's equation for the variation of  $S$ , which does not otherwise differ materially from the Munich observations. It appears that Jakob's excessively high values of  $S$ , have no real foundation in theory or experiment, and are merely due to empirical extrapolation; but since they are confined to the immediate neighbourhood of the saturation line, they produce much less effect than might be expected on the calculated values of  $H$ , and are therefore of little importance in practice, except for special problems involving small differences. This is most easily seen by comparing the values of  $H - H_s$  reckoned from the saturation point at constant pressure up to various degrees of superheat. The whole effect on  $H$  amounts to 0.5 only of a calorie, even at a pressure of 10 kg./cm.<sup>2</sup>, which is beyond the range of Knoblauch and Jakob's experiments, and near the limit of Linde's.

The author's values are seen to be intermediate between those of Linde and Jakob, agreeing with the former near saturation, and with the latter at 250° and 450° C. The rapid increase of Linde's values at high temperatures is chiefly due to the high value of the constant 0.0052, which is equal to  $c$  at 400° C., and is 5 times as great as the author's  $b$ .

The values in the last line are calculated by the aid of the formula

$$H - H_{100} = S_0(t - 100) - a(1 + 0.01P)(4c - 0.0052)P + 2.9, \dots (16)$$

which is not given by Linde, but is easily deduced from his equation.  $H_{100}$  is the value of  $H$  at  $100^\circ$  C. and atmospheric pressure.  $S_0$  is the mean value of  $S$  at zero pressure between  $t$  and  $100^\circ$  C., and is taken from Jakob's tables. The symbols  $a$  and  $c$  have the same values as in Linde's equation (6) on the K.M.C. system. The constant 2.9 is the value of the preceding term at  $100^\circ$  C. and 1 atmosphere.

Table VII. Values of  $H - H_s$  for Superheated Steam at 10 kg./cm.<sup>2</sup> or 142 lbs./in.<sup>2</sup>.

Temp. Cent.	200°	250°	300°	350°	400°	450°
$H - H_s$ , Jakob	12.5	39.3	64.7	89.8	115.1	140.5
" Author	12.0	39.3	65.4	90.8	115.8	140.5
" Linde	12.0	39.5	65.8	91.6	117.3	142.9

The systematic difference between Jakob's values of  $H - H_s$  and those given by either of the characteristic equations, incidentally illustrates the fact that the Munich experiments on  $S$  cannot be reconciled with any reasonable form of characteristic equation unless a special expression for  $S_0$  is employed giving a minimum value somewhere in the neighbourhood of  $200^\circ$  C. There is no experimental evidence for such a minimum, and no theoretical explanation has been suggested. It is most likely that there is a systematic error in the experiments, since all the 2 kg. points are too low, as already remarked, in the region  $150^\circ$  to  $250^\circ$ , as compared with the observations of Regnault (R), and of Holborn and Henning (HS, corrected) at 1 atmosphere, which also probably err in defect.

In any case the differences in the values of  $H - H_s$  for superheated steam at constant pressure are of minor importance as compared with the discrepancies in  $H_s$  according to different formulae. These are illustrated by the following table of values of  $H_s - H_{100}$ , in which the various formulae are extrapolated to  $280^\circ$  C. in order to illustrate more clearly the characteristic differences between them.

The values calculated from Linde's equation show a maximum near  $207^\circ$  C. and fall off much too rapidly at high pressures, owing to the high value of the expression for  $SC$  given by his equation, as previously explained. It follows that the Linde values of  $H$  must also be appreciably too low even at  $120^\circ$  and  $140^\circ$ . But his

equation gives *higher* values at 120° and 140° than Davis's parabola, which must also be too low in this region, though it is distinctly preferable to Linde's at temperatures above 200° C. The values in the line headed Thiesen, are those given by the Davis-Jakob formula, with the value of the critical temperature corrected from 365° to 374° C., which gives improved agreement with values of  $H_s$  below 100° C. It must be remembered in comparing these figures that a difference of half a calorie is less than 1 in 1000 of the value of  $H$ , and is of the same order as the uncertainty of the *absolute* value of  $H$ , but is not without significance in comparing *relative* values over small ranges of temperature.

Table VIII. Values of  $H_s - H_{100}$  according to different formulae.

Temp. Cent.	120°	140°	160°	180°	200°	220°	240°	260°	280°
$H_s - H_{100}$ , Linde	7.2	13.6	18.9	23.0	25.2	25.3	22.2	15.5	3.5
„ Davis	7.1	13.4	18.9	23.6	27.6	30.7	33.0	34.6	35.3
„ Thiesen	7.6	14.5	20.9	26.7	31.7	36.0	39.2	41.5	42.2
„ Author	7.8	14.0	21.3	26.8	31.7	35.8	39.2	41.7	43.0

### 61. The Mean Specific Heat reckoned from Saturation.

According to Regnault's definition of  $H$ , the mean specific heat reckoned from saturation is the factor required for calculating the total heat of superheated steam at any pressure when the degree of superheat is given. The mean specific heat is often tabulated for this purpose, since it affords the only method available if an empirical formula is assumed for  $H$  at saturation. But the method of expression in terms of the degree of superheat is really a survival from the time when the only formula employed was that of Regnault, namely,

$$H = 606.5 + 0.305t_s + 0.48(t - t_s), \dots\dots\dots(17)$$

where  $t_s$  denotes the saturation temperature on the Centigrade scale corresponding to the given pressure. This formula was very simple and convenient for practical purposes, but became inadmissible when it was shown to be inconsistent with measurements of  $H_s$  at low temperatures, and with experiments by the Joule-Thomson method above 100° C.

The method becomes very inconvenient when a complicated empirical formula is employed for  $H_s$ , together with a variable value, requiring elaborate tabulation, for the mean specific heat. Marks and Davis use three different methods for tabulating  $H_s$ .

(1) Between 0° and 100° C., a graphic method representing Smith's

reduction of the observations on  $L$  (II, § 17).<sup>6</sup> (2) Davis's parabolic formula between 100° and 200° C. (3) Above 200° C. a formula of the Thiesen type with  $t_s = 865^\circ \text{C}$ . It would evidently be very difficult to secure a satisfactory degree of continuity in the rate of variation of  $H$ , by such a method. Jakob simplifies the procedure by employing the same Thiesen formula for  $L$  over the whole range, in conjunction with Dieterici's formula for  $h$ , but omits the necessary correction (II, § 13) for  $apv$ .

The values of  $H$  for superheated steam were obtained by Marks and Davis by a step by step numerical integration of a set of curves representing Knoblauch and Jakob's original experiments with slight modifications. It would be difficult to carry out a process of this kind satisfactorily owing to the excessively rapid variation of  $S$  in the neighbourhood of saturation according to Knoblauch and Jakob. The results were smoothed by a graphic process, but cannot be utilised for small differences, or represented by any simple formula, owing to the complexity of the process by which they are deduced, and the impossibility of securing a high order of accuracy of tabulation by such a method.

Knoblauch and Mollier (1911) gave tables and curves of mean and true specific heat, similar to those of Jakob founded on their observations. Their tables differ, however, in two particulars. (1) Their values at saturation from 2 to 8 kg./cm.<sup>2</sup> are from 0.007 to 0.008 higher, owing to the uncertainty of extrapolation, since the lowest observation at 2 kg. was at 160° C. (2) They do not give the extrapolation beyond 8 kg., which, as remarked by Thomas and by Stodola, leads to such curious results on the entropy diagram.

The following table shows a comparison of the values given by Knoblauch and Mollier with those given by the author's formula.

Table IX. Mean  $S$  for Superheated Steam from  $t_s$  to  $t$ , C.

$P =$	2 kg./cm. <sup>2</sup>		4 kg./cm. <sup>2</sup>		6 kg./cm. <sup>2</sup>		8 kg./cm. <sup>2</sup>	
$t_s =$	119.6°		142.9°		158.0°		169.6°	
$t$	K. and M.	Author	K. and M.	Author	K. and M.	Author	K. and M.	Author
150°	0.496	0.513	0.528	0.533	—	—	—	—
200°	0.488	0.505	0.509	0.523	0.537	0.538	0.565	0.558
250°	0.484	0.500	0.499	0.514	0.519	0.528	0.535	0.543
300°	0.482	0.496	0.495	0.508	0.510	0.519	0.521	0.531
350°	0.483	0.493	0.494	0.503	0.505	0.513	0.514	0.522
400°	0.484	0.491	0.493	0.500	0.503	0.508	0.511	0.517
450°	0.486	0.489	0.494	0.498	0.503	0.505	0.510	0.512
500°	0.489	0.487	0.496	0.496	0.504	0.502	0.510	0.508



The differences in the values of  $H - H_0$  deduced from those of  $S_m$  in the above table are unimportant as compared with the uncertainties of the experimental measurements. The maximum difference occurs at  $250^\circ \text{C.}$  and  $2 \text{ kg.}$ , where it amounts to about 1 in 800 of  $H$ . According to the author's view, as previously explained, his own values of  $S_m$  are probably correct in this neighbourhood, but those of Knoblauch and Mollier are systematically too low, as compared with those of Holborn and Henning and of Thomas, in consequence of the defective method employed for the estimation of the heat-loss in their experiments. The author's values are probably a little too high at lower temperatures, and too small at higher temperatures owing to the neglect of the uncertain variation of  $S_0$  with temperature, but the error from this cause is so small and uncertain that it is better to neglect it for the sake of exact consistency with the simple form of adiabatic, as previously explained.

**62. General Expression for  $H$ .** Since the general expression for the variation of the total heat of any substance in terms of  $T$  and  $P$  is

$$dH = SdT - SCdP, \dots\dots\dots(18)$$

it follows that the simplest possible type of expression for the total heat is

$$H = S_0T - SCP + B, \dots\dots\dots(19)$$

where  $S_0$  is taken as constant, and  $SC$  is a function of  $T$  only. While it is permissible to speculate with regard to the effect of other assumptions for the variation of  $S_0$  and  $SC$ , it cannot be said that the experimental evidence at present available in the case of steam justifies the adoption of any more elaborate formula as a standard of reference or for purposes of tabulation.

The thermodynamical formula is just as easy to use for practical purposes as that of Regnault, but has the advantage of greater generality and significance, in addition to giving much better agreement with experiment. Since the pressure and the temperature are the observed conditions defining the state in any practical problem, it appears undesirable to adhere to the artificial method of expression in terms of the degree of superheat, which dates from a time before the first law of thermodynamics was properly understood, and which introduces an unnecessary complication in the calculation. By the aid of the thermodynamical formula, it is much easier to obtain accurate values of  $H$  directly from a table of  $H$  of moderate dimensions, than to calculate such values from

a table of mean specific heat by reference to the degree of superheat. It is difficult by the latter method to secure the degree of accuracy and consistency desirable for comparative purposes without elaborate tabulation.

• When the value of  $H$  itself is required at any particular point, it is generally better to obtain it from the table of  $H$  by interpolation, rather than to calculate it from a table of  $SC$ , as is sometimes recommended. But the Table of  $SC$  (Table IX, Appendix III) will be found useful in some special problems, such as calculating  $S_m$  from the formula

$$S_m = S_0 + P (S'C' - S''C'') / (T'' - T'), \dots\dots\dots (20)$$

at any pressure  $P$  over the range  $T'$  to  $T''$ ; or in deducing the drop of temperature in a throttling process, or for similar purposes involving  $SC$ .

## CHAPTER VII

### ENTROPY AND SATURATION PRESSURE

**63. Available Work, and Carnot's Function.** Many years before the final establishment of the conservation of energy as applied to heat, Carnot, in his famous essay, *Reflections on the Motive Power of Heat* (Paris, 1824), had already enunciated an equally fundamental principle, peculiar to thermodynamics, which he stated as follows:

*"The motive power of heat is independent of the agents set at work to realise it; its quantity is fixed solely by the temperatures between which in the limit the transfer of heat takes place."*

He established this principle by theoretical reasoning which could not be improved materially at the present day. He showed that the action of a heat-engine in obtaining work from heat, could be regarded for theoretical purposes as being equivalent to the repetition of a *cycle of operations* in which the working fluid (e.g. steam) was alternately heated and cooled, serving as the vehicle by which heat was permitted to flow from a high temperature, that of the boiler, to a low temperature, that of the condenser; that work could not be obtained *from heat* in such a process without difference of temperature; and that conversely, wherever a difference of temperature existed, it might be utilised theoretically for the production of motive power. It followed that, when heat was allowed to pass *directly* from one body to another at a lower temperature, by the ordinary processes of conduction, convection, or radiation, without the performance of work, the motive power, which might have been obtained from the same flow of heat through a suitable engine, was wasted. Thus in order to obtain the maximum power from a given flow of heat, it was essential that, in the operation of the ideal engine, *"there should not be any direct interchange of heat between bodies at sensibly different temperatures."* It would not be possible to construct an actual engine satisfying this condition otherwise than approximately. But as Carnot points out, the details of the mechanism are immaterial for theoretical purposes.

In considering the *limit* of possible performance, it is easy to imagine that the theoretical conditions are perfectly satisfied.

The simple Carnot cycle for steam is as follows. The existence of a source of heat, corresponding to the boiler, at a temperature  $T'$ , and of a sink of heat, corresponding to the condenser, at a lower temperature  $T''$ , is postulated. (1) A mixture of water and steam at  $T''$  is compressed in a cylinder, without allowing any heat to escape, until the contents are raised to the temperature  $T'$ . (2) Some of the water is evaporated at  $T'$  by supplying heat from the source which is at the same temperature. (3) The mixture is then expanded without further gain or loss of heat till the temperature falls to  $T''$ . (4) Heat is abstracted by the sink at  $T''$  until sufficient steam is condensed to restore the mixture to its original volume, in which state it must contain the same quantity of heat as it contained originally.

At each repetition of the cycle, a certain quantity of heat  $Q$  is received from the source, a certain quantity is rejected to the sink, and a certain balance of motive power  $W$  is obtained. These quantities could be calculated with great accuracy per unit mass of steam evaporated at  $T'$  from a knowledge of the properties of steam, but the exact values are immaterial for the present purpose. The ideal cycle satisfies the fundamental criterion that there is no interchange of heat between bodies at sensibly different temperatures, all mechanical and thermal losses, such as friction and interchange of heat between the working substance and the walls of the cylinder, are supposed to be absent, and the object is to show that the work obtained per unit of heat supplied must be the maximum that it is possible to obtain *from heat alone*, for any kind of engine, with any working fluid, between the given limits of temperature.

Since the working fluid is at the same temperature as the source during reception of heat, and is at the same temperature as the sink during rejection of heat, an infinitesimal difference of temperature will suffice to reverse the direction of heat-flow in either case. An ideal engine satisfying these conditions would be perfectly reversible so far as the thermal operations were concerned, and would work with equal efficiency in either direction. When taking heat from the source at the high temperature, in the direct method of operation, it would give a certain quantity of motive power  $W/Q$  for each unit of heat supplied by the source; when all its operations were reversed in order and direction, it would abstract heat from the condenser and return it to the source, in

which case the expenditure of the *same* quantity of motive power  $W/Q$  in driving the engine backwards would suffice for each unit of heat returned to the source. Carnot reasoned that the efficiency of such an engine must be a maximum for given limits of temperature, because, if it were possible to devise an engine, or to discover a working fluid, giving more motive power per unit of heat taken from the source, part of the power might be employed to drive a reversible engine backwards and restore to the source the quantity of heat taken from it. We should thus be able to obtain a continuous supply of motive power without any consumption of fuel.

Carnot expressed his principle in the following form for practical application. If  $W$  is the work obtainable with a reversible heat-engine from a quantity of heat  $Q$  supplied to the working fluid at a temperature  $t^\circ \text{C.}$ , the condenser being assumed for simplicity to be at a constant temperature  $0^\circ \text{C.}$ , the efficiency  $W/Q$  must be some function of the temperature only, denoted by  $F(t)$ , giving  $W/Q = F(t)$  as a simple expression of the principle.

The simplest applications of the principle are to cycles of infinitesimal range, for which Carnot employed the equivalent expression

$$dW/dt = QF'(t), \dots\dots\dots(1)$$

deduced by differentiation for a small range of temperature  $dt$ .  $F'(t)$  is the derived function of  $F(t)$ , and is generally known as Carnot's function. It expresses the work obtainable in a cycle per degree fall per unit of heat supplied at a temperature  $t$ , and must be the same for all substances at the same temperature. Its value is easily calculated for any substance when the required physical properties have been determined from experimental data. Carnot verified his principle by calculations of this kind as far as possible with the scanty physical data available at that time. Thus he calculated the value of  $F'(t)$  for steam at  $100^\circ \text{C.}$  in the following manner. He took the latent heat  $L$  required to evaporate 1 kilogram as 550 kilocalories, and the change of volume  $V - v$  from water to steam as 1.70 cb. m. per kg., from Watt's results. In a cycle of  $1^\circ \text{C.}$  range, the forward pressure during evaporation would exceed the back-pressure during condensation by the drop of steam-pressure per degree fall at  $100^\circ \text{C.}$ , denoted by  $dp/dt$ , which he took as being 26 mm. of mercury, or 860 kilos per sq. metre, from Dalton's experiments. The nett work obtainable per kilo, as shown on the indicator diagram, would therefore be

$(V - v)(dp/dt) = 1.70 \times 860 = 611$  kilogrammetres per kg. per  $1^\circ$ . The heat supplied being 550 kilocalories, the work obtainable per  $1^\circ$  fall per unit of heat, or the value of the function  $F'(t)$  for steam at  $100^\circ \text{C.}$ , is

$$F'(t) = (V - v)(dp/dt)/L = 611/550 = 1.12 \text{ kg.m./kilocal.} \dots (2)$$

The value given by the most recent data for steam is 1.144 in the same units.

Carnot found similar values for air and alcohol, confirming his principle, and showing that the value of  $F'(t)$  was probably the same for different substances at the same temperature, but diminished somewhat for all substances with rise of temperature, though he was unable to find the law of variation, owing to the scarcity and inaccuracy of the experimental data available.

The value which he found for air at  $0^\circ \text{C.}$ , though correctly calculated, was far from the truth, and very misleading. The heat absorbed by unit mass of a gas, obeying the law  $PV = RT$ , in expanding by a fraction  $1/T$  of its volume at a constant temperature  $T$ , is equal to the difference  $S_p - S_v$  between the specific heats at constant pressure and volume. Carnot took  $S_p = 0.267$  for air from the experiments of Delaroche and Bérard, and the ratio  $S_p/S_v = 1.43$ , as deduced by Poisson from the velocity of sound, giving 0.080 for  $S_p - S_v$ , in place of the correct value 0.060 according to modern data. The work done in a cycle per  $1^\circ$  fall for the same expansion is  $R/T$ . Carnot took  $T = 267$  at  $0^\circ \text{C.}$  from Gay Lussac's experiments, giving  $R = 30$  kgm. per kg. of air, per  $1^\circ$ , and obtained  $F'(t) = 30/267 \times 0.080 = 1.40$ , whereas it should be 1.568 at  $0^\circ \text{C.}$  His formula gives the expression  $R/T \times F'(t)$  for the difference of the specific heats, which he predicted\* must be the same for equal volumes of all gases at the same temperature and pressure. He also showed that the ratio of the whole work done by a gas in isothermal expansion to the heat absorbed was  $T \times F'(t)$  and was the same† for all. If he could have assumed either to be the same at different temperatures, he would have found that  $F'(t)$  varied as  $1/T$ , but the data were too discordant to suggest the true relation. The missing link was supplied by Joule's experiments at a later date.

Clapeyron (1836) verified Carnot's calculations, and put the expression for  $F'(t)$  in the case of a vapour in the analytical form (2) given above, which is generally known as Clapeyron's equation,

\* Verified by Dulong, 1829.

† Verified by Joule, 1845.

though Carnot was the first to use it for calculating  $F'(t)$ . Clapeyron was the first to employ the indicator diagram for illustrating the performance of an ideal cycle, and to deduce general expressions for  $F'(t)$ , applicable to all substances, in terms of the partial differential coefficients, which are now generally known as the thermodynamical relations (see Appendix I, § 188).

Kelvin (1848) proposed to base an absolute scale of temperature on Carnot's function, since it was the same for all substances at the same temperature, and endeavoured to deduce the relation between  $F'(t)$  and the scale of the gas-thermometer by means of Regnault's experiments on steam. Joule about the same time inferred from the properties of gases that  $F'(t)$  should be simply  $J/T$ . But this was first clearly explained, in terms of the mechanical theory of heat, by Clausius and Rankine (1850), who showed that  $F'(t)$  should be exactly  $J/T$  for a perfect gas, suitably defined by assuming the work done in isothermal expansion equivalent to the heat absorbed, or the difference of the specific heats independent of the temperature, either of which assumptions would make Carnot's expression  $T \times F'(t)$  constant and equal to the mechanical equivalent  $J$ . But there were large discrepancies between the experimental values of  $F'(t)$  and  $J/T$ , and it remained uncertain how far these were due simply to experimental errors or to systematic deviations of actual gases from the properties assumed in defining the perfect gas. This question was attacked by the porous plug method of Joule and Kelvin, who succeeded in showing that the scale of absolute temperature  $T$ , defined in terms of Carnot's function by the relation  $F'(t) = J/T$ , agreed even more closely than could have been anticipated with the gas-scale, especially in the case of the hydrogen thermometer, which has been adopted by general agreement as giving the practical equivalent of the absolute scale of temperature. In this way the relation between the available work and the temperature limits in the Carnot cycle is reduced to the simplest possible form.

**64. The Entropy Measure of Heat.** It follows from Carnot's principle, as above explained, that, when a quantity of heat energy  $Q$  is supplied to any working substance at a temperature  $T$  in a heat-engine, the maximum quantity of work obtainable in a cycle per degree fall is represented by the product  $Q \times F'(t)$ , which is equal to  $JQ/T$  by the definition of absolute temperature. Expressed in heat units, the proportion of the heat energy con-

vertible into work per degree fall is  $Q/T$ , or the quantity  $dQ$  convertible in a range  $dT$  is  $Q(dT/T)$ , or  $(Q/T)dT$ .<sup>o</sup> By the first law, the heat rejected at  $T - dT$  is  $Q - dQ$ .

In a simple Carnot cycle, no heat is received except at the upper limit of temperature  $T'$ , and no heat is rejected except at the lower limit  $T''$ . We may therefore obtain the result for any finite range  $T'$  to  $T''$  by integrating the relation  $dQ/Q = dT/T$ , between limits  $T'$  and  $T''$ , which gives

$$Q'/T' = Q''/T'' = (Q' - Q'')/(T' - T'') = AW/(T' - T''), \dots (3)$$

where  $Q'$  is the heat received at the higher temperature,  $Q''$  the heat rejected at the lower temperature, and  $AW$  the thermal equivalent  $Q' - Q''$  of the work obtainable in the cycle. This method of integration was, in fact, applied by Carnot, and explained (*loc. cit.*, p. 27) as being equivalent to the employment of a series of engines, each working through an infinitesimal range and receiving the caloric rejected by the engine next above it in the series. But the correct expression for the work obtainable in a Carnot cycle of finite range, in terms of heat-energy on the mechanical theory, was first given by Rankine (*Phil. Mag.*, 1851, p. 55).

The thermal equivalent of the work obtainable in a Carnot cycle is seen to be equal to the product of the quantity  $Q'/T'$  (depending only on the heat received and the temperature of reception) and the temperature fall  $T' - T''$ . For a cycle of any form, in which the heat is not all received at one temperature, Rankine showed how to deduce the equivalent of the work obtainable by dividing each elementary quantity of heat  $dQ$  by the temperature of reception  $T$ , multiplying each by the corresponding range of temperature, and summing the results for the cycle. Examples of this method for other cycles are given in Chapter X.

Since the primary object of a heat-engine is to obtain the maximum output of work from heat per degree fall of temperature, it is evident that the quotient  $Q/T$  (or the integral of  $dQ/T$  in the generalised form) is a quantity of great importance in the theory of the heat-engine. Rankine called it the Thermodynamic Function, which is a somewhat vague and inconvenient name. Its properties were more fully investigated by Clausius at a later date, who gave it the name of Entropy, which has been universally adopted.

From many points of view, the entropy  $Q/T$  of a quantity of energy  $Q$  in the form of heat at a temperature  $T$ , may most simply be regarded as being merely a different measure of heat, in terms



of work obtainable per degree fall instead of in terms of total energy. The two measures are equally logical and definite, and are very simply related, but the entropy of a quantity of heat has quite different properties to the energy. The essential difference between the entropy and energy measures of heat is most readily appreciated by analogy with the case of a material fluid. A liquid, like water, is often measured by weight, that is to say, implicitly in terms of the work it is capable of doing per unit fall of level. This method gives a direct measure of quantity, analogous to the entropy measure of heat in terms of work per degree fall of temperature. But we might also measure the total energy possessed by the water in virtue of its elevation, by allowing it to fall to a definite level, and observing the rise of level which it was capable of producing in a known mass by any suitable mechanism. This would be analogous to the measurement of the total energy of a quantity of heat by observing the rise of temperature it was capable of producing in a calorimeter of known thermal capacity. Entropy is sometimes called "heat-weight" on the ground of the first analogy, and is the most appropriate measure of heat *quantity* as distinct from heat *energy*, but there is no simple method of measuring it directly. Thus, when a quantity of heat-energy  $Q$  is allowed to pass from a hot body at a temperature  $T'$  to a calorimeter at a temperature  $T''$ , the gain of *energy* of the calorimeter is equal to the loss of energy of the hot body, by the law of conservation of energy, and is easily measured. But this is not true of the entropy. The gain of entropy  $Q/T''$  of the calorimeter is necessarily *greater* than the loss of entropy  $Q/T'$  of the hot body, because  $T'$  is by hypothesis greater than  $T''$ . If the heat-energy  $Q$  had been supplied to a Carnot engine at  $T'$ , the entropy of the heat rejected at  $T''$  would have been equal to that of the heat supplied, namely  $Q/T'$ ; and the heat-energy rejected would have been reduced by the thermal equivalent of the work utilised, namely  $Q(T' - T'')/T'$ . When the heat  $Q$  is allowed to flow directly from  $T'$  to  $T''$ , without performance of work, the increase of entropy, namely  $Q/T'' - Q/T'$ , is the equivalent of the available work divided by  $T''$ , and is the same as if the work had actually been realised and then converted into heat by friction at the lower temperature.

The properties postulated for caloric on the older theory were similar in most respects to those of entropy, but did not correspond with those of heat measured as *effergy* in a calorimeter. This naturally led to grave difficulties in connection with the theory of gases,

and of heat generated by friction. Fortunately it did not affect the validity of Carnot's reasoning, which, though expressed in the language of the caloric theory, was in the main independent of any assumption as to the nature of heat or the manner in which it was measured. (*Proc. Phys. Soc.* 23, p. 153, 1911.)

Heat is always measured as *energy* in practice, and the corresponding changes of entropy are inferred by dividing each addition of heat in thermal units by the temperature at which it is received. The entropy of a substance in any state is reckoned per unit mass from a standard state selected as the zero of entropy for the substance. The numerical values obtained in this way as representing the entropy of a substance, are independent of the temperature scale and the unit of mass, and are the same in all rational systems of units. The unit of entropy is often called a "Rank," after Rankine, but the name is seldom required, because there is practically only one unit of zero dimensions, so that troublesome questions of conversion or nomenclature do not arise.

**65. Properties of the Entropy.** The most important properties of the entropy for the present purpose are as follows:

The entropy of a body remains constant when no energy in the form of heat is lost or gained, a condition usually implied by the term "adiabatic." It is not altered by the performance of external work in adiabatic expansion or compression, provided that there is no internal friction. If there is any friction between parts of the substance moving with different velocities, or between the body considered and neighbouring bodies, the increase of entropy is the thermal equivalent of the work wasted in friction divided by the absolute temperature.

If there is any interchange of heat between different parts of the body at different temperatures, the effect is always to increase the entropy of the whole. For any direct transfer of heat-energy  $Q$  from a part at a temperature  $T'$  to a part at a lower temperature  $T''$ , the increase of entropy is  $Q/T'' - Q/T'$ , which is necessarily positive.

We have already seen that, in a simple Carnot cycle, the entropy of the heat received  $Q'/T'$  is equal to the entropy of the heat rejected  $Q''/T''$ . The same proposition is true for a cycle of any form, provided that it is reversible. This condition is tacitly assumed for any cycle represented on the indicator diagram, since the state of the working fluid is supposed to be one of equilibrium

at uniform pressure and temperature throughout its substance, and the absence of internal friction is assumed. Such a cycle may be regarded as being built up of elementary Carnot cycles by supposing the area divided up into strips by a family of adiabatic curves. For each of the elementary cycles the entropy of the heat received is equal to that of the heat rejected. The whole entropy received in the cycle is therefore equal to the entropy rejected.

It follows that the increase of entropy of a substance per unit mass in any given change of state must be independent of the manner in which the change is effected. For suppose the change from the state  $A$  to the state  $B$  effected in any manner, and the reverse change from  $B$  to  $A$  in a different manner. The two paths on the indicator diagram represent a closed cycle, such that the entropy received along one is equal to that rejected along the other. This does not apply to heat measured as energy. The energy of the heat received along  $AB$  would differ by the equivalent of the enclosed area from that rejected along  $BA$ .

**66. Entropy of Water and Steam at Saturation.** The entropy of dry saturated steam, denoted by  $\Phi_s$ , exceeds that of water, denoted by  $\phi$ , at the same temperature and pressure, by the entropy of vaporisation  $L/T$ , which is obtained by simply dividing the latent heat of vaporisation by the absolute temperature, since all the heat is added at one and the same temperature.

The entropy of vaporisation may also be expressed as the equivalent of the work obtainable per degree fall per unit mass vaporised, namely  $a(V_s - v) dp/dt$ . Combining the two methods of expression, we obtain the equation

$$\Phi_s - \phi = L/T = a(V_s - v) dp/dt, \dots\dots\dots(4)$$

which is the modern form of Clapeyron's equation, and represents the direct application of Carnot's principle as previously explained.

In the past, this equation has generally been employed for deducing the volume of dry saturated steam from the observed values of  $L$  and of  $dp/dt$ . But if the variation of  $V$  with temperature and pressure can be deduced from other experiments, such as those on the cooling-effect, Clapeyron's equation may be employed for calculating the values of the saturation pressure  $p$ , as explained later in § 68.

If the steam is wet, consisting of a fraction  $q$  (called the quality, or the dryness-fraction) of dry steam per unit mass with a fraction

$1 - q$  (called the wetness-fraction) of fine particles of water in suspension, the entropy  $\Phi_q$  of the wet mixture is

$$\Phi_q = \phi + qL/T = \Phi_s - (1 - q)L/T. \quad \dots\dots\dots(5)$$

The corresponding expressions for the total heat and volume are

$$H_q = h + qL = H_s - (1 - q)L, \quad \dots\dots\dots(6)$$

$$V_q = (1 - q)v + qV_s = V_s - (1 - q)(V_s - v), \quad \dots\dots\dots(7)$$

where  $H_s$  and  $V_s$  are the total heat and volume of dry saturated steam at the same pressure. But, unless  $q$  is given, it is generally preferable to calculate  $\Phi_q$  and  $V_q$  directly from  $H_q$  (which is the quantity given by experiment) by means of the relations

$$\Phi_s - \Phi_q = (H_s - H_q)/T, \quad \dots\dots\dots(8)$$

$$V_s - V_q = V_s(H_s - H_q)/(H_s - st), \quad \dots\dots\dots(9)$$

which are exact, and save reference to  $q$ ,  $h$ ,  $v$ ,  $\phi$ , and  $L$ .

If the total heat of water  $h$  at saturation pressure and temperature is represented by the expression already given, equation (6) in Chapter II, namely,

$$h = 0.99666t + vL/(V - v) - 0.003, \quad \dots\dots\dots(10)$$

the corresponding expression for the entropy of water  $\phi$  under saturation pressure reckoned from  $0^\circ \text{C.}$ , is

$$\phi = 2.2949 \log_{10} T/273.1 + vL/T (V - v) - 0.00001, \quad \dots\dots\dots(11)$$

The first term is obtained by integrating  $0.99666/T$  from  $273.1$  to  $T$ . The second term is the entropy of vaporisation of the steam molecules in the water. The small constant  $0.00001$  is the value of this term at  $0^\circ \text{C.}$

It should be remarked that the correspondence of these two formulae for  $h$  and  $\phi$  is thermodynamically *exact*, and that the entropy of water at saturation cannot be deduced from the total heat  $h$  at saturation correctly by differentiating the formula for  $h$ , dividing by  $T$ , and integrating the expression for  $(dh/dt)/T$ , as is usually done, because  $(dh/dt)_s$  is not equal to  $T(d\phi/dt)_s$ , as commonly assumed, but is greater by the term  $av(dp/dt)$ . The difference is most readily appreciated by comparing the corresponding formulae for the vapour (see Appendix I, §§ 181-2). The value of  $(dH/dT)_s$  for steam is relatively small and positive, but that of  $T(d\Phi/dT)_s$ , the "saturation specific heat," is large and *negative*, being less than  $(dH/dT)_s$  by the expression  $aV(dp/dt)$ , as in the

case of the liquid. The error due to neglecting this term in the case of the liquid is relatively small, but the corresponding term  $avT (dp/dt)$  in  $T\phi$  is from 10 to 20 times larger than the term  $apv$  representing the feed-pump work in the Rankine cycle, upon which so much stress is usually laid. The distinction between  $(dh/dt)_s$  and  $T (d\phi/dt)_s$  is of essential importance in the author's definition of  $h_s$  (E. B., 1902), because the corresponding expression for  $\phi_s$  will not integrate exactly if Gray's definition (Chapter II, § 12) is adopted, or if the term  $av (dp/dt)$  is neglected. On subtracting  $av (dp/dt)$  from  $(dh/dt)_s$  and dividing by  $T$ , the expression for  $(d\phi/dt)_s$  becomes an exact differential, and gives between limits,

$$\phi_s = s \log_e (T/T_0) + av (dp/dt) - av_0 (dp/dt)_0, \dots (12)$$

which is exactly equivalent to the above numerical formula. Since  $h$  and  $\phi$  for the liquid are required only at saturation, the suffix  $s$  can usually be dropped.

The entropy of water at 100° C. by (11) is  $\phi_1 = 0.31186$ .

The entropy of vapourisation at 100° C. is  $L_1/T_1 = 1.44546$ .

**67. Expression for the Entropy of Dry Steam, Superheated or Supersaturated.** The general expression for the entropy of dry steam at any temperature  $T$  and pressure  $P$  is readily deduced from that of dry saturated steam in any given standard state (preferably at  $T_1 = 373.1^\circ\text{C}$ . and standard atmospheric pressure  $P_1$ , at which point  $\Phi_1 = 1.75782$ , by (4)), by the aid of the characteristic equation, and the general expression for the specific heat  $S$ . The entropy added in superheating the steam at constant atmospheric pressure  $P_1$  from  $T_1$  to  $T$ , is the integral of  $S_1 dT/T$ , where  $S_1$  has the value  $S_0 + an(n+1)cP_1/T$ . The entropy subtracted in compressing the steam at constant temperature  $T$  from  $P_1$  to the final pressure  $P$ , is the integral of the expression  $(R/P + anc/T) dP$ , or  $a(dV/dt)_s dP$ . Performing these simple integrations we obtain

$$\Phi - \Phi_1 = S_0 \log_e T/T_1 - R \log_e P/P_1 - ancP/T + anc_1P_1/T_1, \dots (13)$$

The variation of the entropy of steam is the same as that of a perfect gas with the addition of the small term depending on the coaggregation  $c$ . Putting in the known values of the constants, and reducing the logarithms to the base 10, we obtain

$$\Phi = 1.09876 \log_{10} T/T_1 - .25356 \log_{10} P/P_1 - ancP/T + 1.76800, \dots (14)$$

It is better to keep the formula for  $\Phi$  in terms of the ratios  $T/T_1$  and

$P/P_1$  for calculation, because  $\log T/T_1$  is small compared with  $\log T$ , and some trouble is saved in interpolating the logarithms. There is no physical meaning in referring the entropy to an arbitrary standard state such as  $T = 1^\circ \text{abs.}$  and  $P = 1 \text{ lb./sq. in.,}$  or 1 mm. of mercury, as is commonly done. With the above formula, the constant 1.76800 is the entropy at  $100^\circ \text{C.}$  in the state of ideal gas, and exceeds the entropy of dry saturated steam at  $100^\circ \text{C.}$  by the value of the small term  $anc_1 P_1/T_1$  which is .00568.

Since  $c$  varies as  $1/T^n$ , the small term varies as  $P/T^{n+1}$ , and since  $S_0 = (n+1)R$ , the expression for the entropy may be put in the form

$$\Phi = R \log_e X_1/X - anc_1 P_1 X/T_1 X_1 + 1.76800, \dots (15)$$

where  $X = P/T^{n+1}$ , and  $X_1 = P_1/T_1^{n+1}$ , which shows that the entropy is constant when  $P/T^{n+1}$  is constant. Eliminating  $P$  or  $T$  by the aid of the characteristic equation, the equation of the adiabatic may also be put in any of the following forms,

$$\left. \begin{aligned} & (V-b) T^n = \text{constant} \\ \text{or} & P(V-b)/T = \text{constant} \\ \text{or} & P^n (V-b)^{n+1} = \text{constant} \end{aligned} \right\}, \dots (16)$$

which are exact, and are often more convenient than the expression for  $\Phi$ , when the initial state is given by  $P$  and  $T$ , or  $P$  and  $V$ , or  $V$  and  $T$ , and it is required to find the final state, given  $P$ , or  $T$ , or  $V$ , after expansion.

**68. Equation of Saturation Pressure.** The general expression above found for the entropy of dry steam in any state must agree with the expression  $\phi + L/T$ , previously given for dry saturated steam in terms of the latent heat, not only at  $100^\circ \text{C.}$  (where the agreement is assumed in finding the value of the constant 1.763), but also at every point of the saturation curve, when the correct values of  $p$  and  $T$  are inserted in the expression. The condition obtained by equating the two expressions for the entropy represents, in fact, the equation of saturation pressure, or the relation between  $p$  and  $T$  in the saturated state, from which the saturation pressure  $p$  is easily calculated for any given value of  $T$ .

Thus if we substitute  $\Phi = \phi + L/T$  in the general expression (18), in which  $\Phi_1$  represents  $\phi_1 + L_1/T_1$ , we obtain

$$\phi - \phi_1 + L/T - L_1/T_1 = S_0 \log_e T/T_1 - R \log_e p/p_1 - anc p/T + anc_1 p_1/T_1, \dots (17)$$

where the values at  $100^\circ \text{C.}$  are denoted by the suffix 1.

The value of  $p$  might be calculated by trial from this equation, but it would be inconvenient because  $\phi$  and  $L$  both involve  $p$  implicitly, in addition to the terms  $R \log_e p/p_1$  and  $anep/T$ . We accordingly substitute for  $\phi$  from (12), with  $L = H_s - h$ , from equations II (5) and III (24). With these substitutions, most of the small terms eliminate, and the remainder collect in a convenient manner, giving the required equation in the form

$$\bullet \quad R \log_e p/p_1 = L'(t-100)/TT_1 + (S_0 - s)[\log_e T/T_1 - (t-100)/T] \\ + [a(c-b)p/T]_{100}^t, \dots\dots(18)$$

where the last term is to be taken between limits 100 and  $t$ . The constant  $L'$  represents the ideal value 542.37 of the latent heat at 100° C., which is equal to the actual value  $L_1 = 539.30$ , together with the latent heat of the steam molecules in the water, namely  $vL/(V-v) = 0.337$ , and the water molecules in the steam, namely  $SCp = 2.733$ , both reckoned at 100° C. and saturation.

It will be observed that this form of the theoretical equation of saturation pressure is the simplest possible, since it differs from that of an ideal liquid and vapour as given by Rankine (*Phil. Mag.*, 1866) only by the addition of the term  $a(c-b)p/T$ . It remains true if  $c$  is any function whatever of the temperature only, and is not restricted to the special case  $c = kT^{-n}$ . If  $c$  is a function of  $P$  as well as  $T$ , it is merely necessary to replace the last term by the integral of  $a(c-b)dP/T$  at constant  $T$ , taken between limits.

The object of putting the equation of saturation pressure in this form is twofold. In the first place the terms depending on the fundamental constants (the specific and latent heats, and the coaggregation), are separated, so that the effect of experimental errors on the determination of each can be more easily investigated. In the second place, it is more convenient for calculation, because all the terms except the first are small, and can be worked out with a Fuller slide-rule, or with five-figure logarithms. Reducing to common logarithms by the modulus  $m = .4342945$ , and inserting the numerical values of the constants, the equation becomes

$$\log p/p_1 = 18.2009m(t-100)/T \\ - 4.7173[\log T/T_1 - m(t-100)/T] + [.4057(c-b)p/T]_{100}^t \dots\dots(19)$$

In working out the value of  $p$  for any given  $t$ , the term  $m(t-100)/T$  is calculated by logarithms. The first term (1) in the equation is found by adding  $\log 18.2009 (= 1.26048)$  to the

log of  $m(t - 100)/T$  already found and taking the antilog. The second term (2) by multiplying the small difference

$$\log T/T_1 - m(t - 100)/T$$

by 4.7173 with a Fuller slide-rule. The last term (3), which is of the same order of magnitude as the second, is also worked on the slide-rule, assuming an approximate value of  $p$ , and taking  $(c - b)$  from a table. The constant value of this term at  $100^\circ \text{C.}$  is .006474 (4), which is subtracted from the value found. The value of  $\log p_1$  is added, taking  $p_1$  in mm. of mercury, or lbs./sq. in. or kilos./sq. cm., according to the units in which  $p$  is required. The work may conveniently be arranged as follows:

Pressure at  $t = 250^\circ \text{C.}$ ,  $T = 523.1^\circ \text{abs.}$ ,  $c - b = 0.12054 \text{ cu. ft.}$ ,  
 Trial value  $p = 560 \text{ lbs./sq. in.}$  Result  $p = 564.94$ .

$\log m =$	1.6377843	$\log T =$	2.7185847	$\log p_1 =$	1.16699
$\log 150 =$	2.1760913	$\log T_1 =$	2.5718252	(1) =	1.64397
$\log T =$	- 2.7185847	Diff. =	0.1467595	(3) =	0.05235
Sum =	1.0952909	= log	0.1245348	(4) =	- 0.00647
Add	1.1206043	Diff. =	0.0222247	$\times 4.7173 =$	(2) = - 0.10484
Sum =	.2158952	= log	1.64397 (1)	$\log \bar{p} =$	2.75200

Taking  $p = 570$  as trial, alters term (3) to .05329, whence  $\log p = 2.75294$ , or  $p = 566.16$ . A difference of 10 lbs. in the trial value makes a difference of 1.22 lbs. in the result. Let the correct answer be  $560 + x$ . Then we have  $560 + x = 564.94 + 0.122x$ , or  $0.878x = 4.94$ ,  $x = 5.63$ . Whence finally,  $p = 565.63$ .

For temperatures near  $100^\circ \text{C.}$  the small terms are much smaller, and the approximation is more rapid.

The numerical formula for the saturation pressure in lbs. per sq. in. (London) may easily be transformed into the apparently simpler shape

$$\log p = 21.07449 - 2908.39/T - 4.71734 \log T + .4057 (c - b)p/T, \quad \dots (20)$$

but the terms are much larger, and, since the result depends on small differences, the formula must be worked to the limit of accuracy with seven-figure logarithms. The term involving  $\log T$  is more than 100 times larger than in the formula previously given, even at  $250^\circ \text{C.}$ , so that most careful interpolation is required to get the value of  $\log p$  correct to five places of decimals, or  $p$  to 1 in 40,000.



An instructive method of deducing the formula is by the direct integration of Clapeyron's equation (4). This equation may be written in the form

$$aT(V_s - v)(dp/dT) = L. \dots\dots\dots(21)$$

Since  $L = H - h$ , and  $h = st + v(dp/dT) - 0.003$ , the equation becomes

$$aTV_s(dp/dT) = H_s - st + 0.003. \dots\dots\dots(22)$$

Substituting for  $V_s$  and  $H_s$  from equations (21) and (24) of Chapter III, and dividing by  $T^2$ , the equation is found to be the exact differential of that already given, with a slight difference in the arrangement of the terms.

### 69. Gibbs' Function or Thermodynamic Potential $G$ .

It will be observed that the above substitution in Clapeyron's equation gives an expression for the total heat  $H_s$  of saturated steam identical in form with that already assumed for the total heat  $h$  of water at saturation. The only difference is that  $v$  is replaced by  $V_s$ , thus

$$H_s = st + aTV_s(dp/dT) - 0.003. \dots\dots\dots(23)$$

It follows, by exactly similar reasoning, that the entropy  $\Phi_s$  of saturated steam can be represented by an expression corresponding to that for  $\phi$ , namely,

$$\Phi_s = s \log_e T/T_0 + aV_s(dp/dT) - 0.000010. \dots\dots\dots(24)$$

The value of the function  $G_s = T\Phi_s - H_s = T\phi - h$ , is the same for water and steam at saturation, since  $\Phi_s - \phi = L/T$ . With the assumption already made for the variation of the specific heat of water, the function  $G_s$  has the comparatively simple expression

$$G_s = T\Phi_s - H_s = T\phi - h = s(T \log_e T/T_0 - t) - 0.003t/T_0. \dots\dots\dots(25)$$

This is a function of the temperature only, and is very easily tabulated. It is particularly useful in the adiabatic expansion of wet steam (see p. 213).

The name "Potential" is here given to the function  $G = T\Phi - H$  because equality of potential  $G$  may be regarded as the condition of equilibrium between liquid and vapour at any temperature. The properties of this function, as the criterion of equilibrium in physical and chemical changes, were first fully investigated by Willard Gibbs (*Trans. Acad. Conn.*, vol. 3, p. 108, 1875-1878). It is often called the Gibbs' function, and is denoted by various Greek or fancy-script symbols in different works. The symbol  $G$  is here adopted

as being the initial of the name Gibbs, on which ground it was recommended to the Physical Society of London, and by them adopted in their list of symbols for thermal properties.

In many books the total heat  $H$  is also called "the potential," on the analogy of potential energy in statics, because the drop of total heat represents the work done in steady flow at constant entropy. The objection to this analogy is that the potential energy of the fluid depends on the conditions imposed, and that many different functions possess an equal right to the title of potential functions on this ground. Thus the increase of the function  $G$ , as here defined, represents the work obtainable in steady flow when the temperature is kept constant. The work so obtained is the maximum obtainable from unit mass of compressed gas at atmospheric temperature without expenditure of fuel, and might most appropriately be regarded as equivalent to the drop of potential energy on expansion. Mathematicians often define  $G$  as  $H - T\Phi$ , with the opposite sign, as representing a drop of energy. But the sign is purely a matter of convention, and it is just as logical to regard the increase of  $G = T\Phi - H$  in an irreversible process as corresponding to the increase of  $\Phi$ . It would also be very inconvenient in practice to have the sign of  $G$  always negative.

The expression for the potential  $G$  of dry steam, superheated or supersaturated, is readily obtained from those already given for  $H$  and  $\Phi$ , thus

$$G = S_0 T \log_e (T/T_1) - RT \log_e (P/P_1) + a(c-b)P + (\Phi_0 - S_0)T - B, \quad \dots\dots(26)$$

where  $\Phi_0 = 1.76300$ , and  $B = 464.00$ , the constants in the expressions for  $\Phi$  and  $H$ .

If the above expression for  $G$  is equated to the expression already given for  $G$ , in the case of water, we obtain immediately the equation of saturation pressure, which is readily reduced to the form previously given.

The potential  $G$  of superheated steam is always greater than that of water. When it becomes equal to that of water at the same temperature, the steam will begin to condense, if any suitable surfaces or nuclei are present to start the condensation. It is well known, however, that steam may be obtained by rapid expansion in the supersaturated condition, at a temperature much lower than the saturation temperature corresponding to the pressure, provided that no nuclei are present. Its potential in this condition is given

by the same expression as that for superheated steam, but is lower than that of water at the same pressure. The state of supersaturated steam is unstable, and is quickly reduced to that of wet saturated steam as soon as condensation sets in. The transformation of supersaturated steam into wet steam is an irreversible process, involving an increase of entropy, which must always occur in rapid expansion because the condensation cannot keep pace exactly with the adiabatic fall of temperature. Some evidence of the actual existence of this supersaturated state in the cylinder of a steam-engine was obtained by Callendar and Nicolson (*Proc. Inst. C. E.*, 1898) by measuring the temperature with a platinum thermometer during rapid expansion. The phenomenon is of practical interest as explaining part at least of the "missing quantity," and some of the advantage gained by superheating. When the steam is initially superheated, the state of supersaturation is postponed to a later point in the stroke, and the increase of entropy is reduced. Since the state of supersaturation undoubtedly exists, the tables have been extended a little below the saturation line. The values for supersaturated steam are of practical significance, as showing the nature of the change which occurs in rapid expansion when the steam has insufficient time to condense, and as affording a means of estimating the losses thereby occasioned. The best illustration of the effects of supersaturation is afforded by the flow of steam through a nozzle, where the expansion is extremely rapid (see Chapter X).

#### 70. Experimental Values of the Saturation Pressure $p$ .

Since all the required quantities in the equation of saturation pressure have been determined independently of any measurements of the saturation pressure itself (except that the saturation pressure is 760 mm. by definition at  $100^{\circ}$  C.), the comparison of the values of  $p$  calculated by equation (19) with those directly observed, affords an additional test of the accuracy of the theory. A comparison of this kind was made in the author's original paper (*R. S.*, 1900) with the observations of Regnault, which were the best then available, and the agreement was shown to be satisfactory. Since that time additional determinations have been made, with modern appliances, at Munich (1905) by Knoblauch, Linde and Klebe (*Forsch. Ver. Deut. Ing.*, 21), and at the Reichsanstalt, Berlin (1908) by Holborn and Henning (*Ann. Phys.*, 26, pp. 833-888). The results of these observations, as expressed in

mm. of mercury (Lat.  $45^\circ$ ), are compared with the author's equation in the following table.

Table I. Comparison of (19) with Observations of the Saturation Pressure.

Temp. Cent.	Regnault Formula ( $H$ )	Author's equation	Münich (1905)	Berlin (1908)
$0^\circ$	4.48	4.02	—	(4.58)
$20^\circ$	17.30	17.59	—	(17.51)
$40^\circ$	54.91	55.38	—	(55.13)
$60^\circ$	148.83	149.38	—	149.19
$80^\circ$	354.6	355.1	—	355.1
$110^\circ$	1075.4	1075.0	1074.3	1074.5
$120^\circ$	1491.3	1490.5	1489	1488.9
$130^\circ$	2030.3	2028.8	2025	2025.6
$140^\circ$	2717.6	2715.3	2710	2709.5
$150^\circ$	3581.2	3577.7	3567	3568.7
$160^\circ$	4652	4646	4634	4633
$170^\circ$	5962	5953	5939	5937
$180^\circ$	7546	7532	7514	7514
$190^\circ$	9443	9420	—	9404
$200^\circ$	11689	11653	—	11647

The agreement between the observed and calculated values shown in the above table is seen to be extremely close, and affords in fact one of the most exacting practical tests of the second law of thermodynamics, on which the calculation is based. The discrepancies rarely amount to as much as a tenth of  $1^\circ$  C., or 1 in 2000 of the temperature interval, except in the case of Regnault's observations at low temperatures, which are known to be inexact. The agreement with the Berlin observations below  $100^\circ$  C. is much closer than with Regnault's formula. The values at  $0^\circ$ ,  $20^\circ$ , and  $40^\circ$  C., enclosed in brackets, are those given by Thiesen and Scheel (*Wiss. Abh. d. Reichs.*, 3, p. 71, 1900), which have been adopted by Holborn and Henning in their table.

Above  $100^\circ$  C., the author's results are intermediate between those of Regnault and those of the later observers, agreeing better with Regnault from  $100^\circ$  to  $180^\circ$  C., but approaching the later observers at  $200^\circ$  C. The close agreement between the values tabulated by the Munich observers (1905) and those subsequently determined by Holborn and Henning, Berlin (1908), is one of the most remarkable coincidences in experimental physics. The conclusion has not unnaturally been drawn that both of the later series of observations must be very exact, and that the systematic

discrepancy from the author's equation, equivalent to about a tenth of  $1^\circ$  C. from  $150^\circ$  to  $180^\circ$  C., is to be explained by some error in the theory. It happens, however, that Henning (*Ann. Phys.*, 22, p. 825, 1907) has made an independent reduction of the Munich observations, and has found a different set of values for  $p$  (Münich) which are in exact agreement with the author's equation from  $120^\circ$  to  $180^\circ$  C. The discrepancy is of little practical importance, but is of theoretical interest as throwing further light on the curious discontinuity at  $100^\circ$  C. in Henning's curve of  $H$ , already illustrated in Fig. 4, which appeared to be so well supported by the Munich observations as reduced by Linde. In order to be able to form a fair estimate of the value of the experimental evidence, it is desirable to plot the separate observations of  $p$  in relation to the curves representing the formulae, as shown in the annexed Fig. 13.

In place of plotting the differences of pressure as shown in the table, it is better to plot the corresponding differences of temperature, because the errors above  $100^\circ$  C. are mainly due to thermometry, and because a more convenient scale is thereby obtained. Thus if  $p_0$  is the observed pressure, and  $p_a$  the pressure given by the author's equation at the same temperature, the small difference  $p_0 - p_a$  is divided by the appropriate value of  $dp/dt$ , giving the corresponding difference of temperature, which is plotted with its proper sign against the temperature of observation.

The zero line 00 in the figure represents the author's equation. The curve RR represents Regnault's formula  $H$ . The wavy line marked HH represents Holborn and Henning's table. The wave at the lower

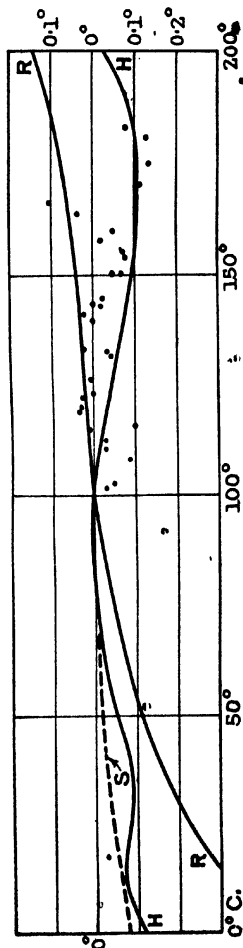


Fig. 13.  $p$ ,  $0^\circ$ — $200^\circ$ .

extremity represents the observations of Thiesen and Scheel. It would be of no use to plot Regnault's observations on this scale, since the points would give a diffuse band,  $0.8^\circ$  to  $0.4^\circ$  wide, nearly filling the figure. The majority of his observations lie below the line RR between  $100^\circ$  and  $200^\circ$ , and above the line RR between  $0^\circ$  and  $100^\circ$ , showing on the whole better agreement with the author's equation than with his own formula.

The dots plotted above  $100^\circ$  C. represent the Munich observations, which evidently give better agreement with the author's equation than with the line HH, except for the last four, which were too near the limit of satisfactory performance of the apparatus, and also gave unreliable results for the volume. The discrepancies indicated by the scattering of the dots were no doubt largely due to the employment of mercury thermometers, which showed irregularities of the order of 1 or 2 tenths of a degree, as is usual at such temperatures with mercurial thermometers.

The observations of Holborn and Henning on the other hand, appear to have been extremely concordant. They employed platinum thermometers for measuring the temperature, and an electric heating coil for vaporisation. Their apparatus could scarcely fail to give *consistent* results in capable hands, but was of a type peculiarly liable to systematic errors from radiation and conduction, so that it is questionable whether the temperature which they measured was the actual temperature of the steam. The proximity of the electric heater to the tube containing the thermometer, might easily give rise to small systematic errors of the order of a tenth of  $1^\circ$  C. It is most likely that the observed temperatures would be systematically too high (or the corresponding pressures too low) since temperature-errors in defect would be prevented by the condensation of the steam. A systematic error of precisely this type is indicated by the somewhat abrupt fall of the curve HH starting from the  $100^\circ$  point. The abrupt change of curvature at  $100^\circ$  C. is better shown in the difference curve representing Holborn and Henning's observations in their original paper, where the temperature differences are plotted on a four times larger scale. It is obviously due to a systematic error of observation of the kind described, since no possible reason for an abrupt change at  $100^\circ$  C. can be found in theory. The existence of a systematic error in the values of  $dp/dt$  is further corroborated by the fact previously alluded to (Chapter V, § 46), that the values of  $L$  calculated by Linde from the Munich values of  $V$  and  $dp/dt$  agreed so remarkably with those

subsequently given in Henning's table, and gave a similar abrupt and impossible bend in the curve of  $H$ , at  $100^{\circ}$  C. as shown in Fig. 4. The values of  $dp/dt$  employed by Linde were practically identical with those subsequently found by Holborn and Henning. Whereas if Henning's reduction of the Munich observations on  $\beta$  is accepted, the abrupt bends in the  $H$ , and  $p$  curves disappear, and both are brought into very close agreement with the author's, and with the theoretical expression for  $H$  derived from Linde's equation. The systematic error of Holborn and Henning's table of  $p$  ( $H$  and  $H$ ), though small, is of theoretical importance on account of its effect on the calculation of  $L$  from  $V$ ; because, when taken in conjunction with Henning's low values of  $L$  between  $120^{\circ}$  and  $160^{\circ}$  C., it has led nearly all recent computers to depress the  $H$ , curve unduly in this region, and to employ the erroneous value  $t_0 = 365^{\circ}$  for extrapolation in the Thiesen formula.

The broken line marked S in the figure below  $100^{\circ}$  C. indicates the effect of assuming the variable value,  $S_0 = 0.460 + 0.0001t$ , in place of the constant value,  $S_0 = 0.4772$ , in calculating the saturation pressure. This assumption makes so little difference to the curve between  $100^{\circ}$  and  $200^{\circ}$  that it could hardly be shown on the scale of the figure. At low temperatures, it appreciably improves the agreement with experiment, but the pressure differences are here so small that it is of no practical importance. It must also be remembered that the adoption of the variable value of  $S$  impairs the agreement with Griffiths' and Dieterici's values of  $L$ , and complicates all the equations unnecessarily for practical purposes.

The experimental values of  $p$ , and *a fortiori* those of  $dp/dt$ , are probably less accurate than the calculated values between  $100^{\circ}$  and  $180^{\circ}$  C., where the data for the calculation are satisfactory. The uncertainty of both increases rapidly at higher temperatures, but it appears probable that the calculated values are sufficiently accurate for most practical purposes up to  $250^{\circ}$  C., where the error of the formula (19) cannot exceed  $1^{\circ}$  C., and is probably much less.

**71. Methods of Interpolation for tabulating  $p$ .** In constructing consistent tables of the properties of saturated steam, the first essential is to calculate the values of the saturation pressure for different temperatures by means of the theoretical equation (19), already given. The other properties are then easily determined by inserting corresponding values of the pressure and

temperature in the equations for dry steam. It is commonly objected to the author's theoretical equation for the saturation pressure that it is too complicated for practical use, and cannot easily be inverted so as to give the temperature in terms of the pressure. Many attempts have been made to devise empirical formulae with this object, but without much success. When however it is a question of interpolation over a restricted range, such as  $10^\circ$ , a formula of interpolation may readily be deduced from the original equation. A formula of this kind is useful, because the ordinary method of interpolation by simple proportion is unsatisfactory in dealing with the saturation pressure or volume, unless the differences involved are very small. Interpolation by taking the logarithm of the pressure in place of the pressure itself is often recommended, and gives results about five times as accurate as the method of simple proportion over a range of  $10^\circ$ . But the following rule, deduced from the pressure formula itself, is very little more trouble than logarithmic interpolation, and is about ten times more accurate.

*Rule.* Given the pressures  $p'$  and  $p''$  corresponding to temperatures  $t'$  and  $t''$  in the tables, to find the value of  $t$  corresponding to any intermediate pressure  $p$ , find  $t - t'$  by logarithmic interpolation, reduce it in the ratio  $T/T''$ , and add the result to  $t'$ .

The ordinary rule of linear interpolation by simple proportion gives

$$t - t' = (t'' - t') (p - p') / (p'' - p'). \dots\dots\dots(27)$$

Logarithmic interpolation gives

$$t - t' = (t'' - t') (\log p - \log p') / (\log p'' - \log p'). \dots(28)$$

This is worked on the slide-rule, and reduced in the ratio  $T/T''$ .

The explanation of this rule for inverse interpolation follows immediately from the form of the equation of saturation pressure, namely,

$$\log p/p' = 18.2m (t - t')/T + \text{small terms}, \dots\dots\dots(29)$$

since the second term  $\log T/T' - m (t - t')/T$  in the equation is small when  $t$  is nearly equal to  $t'$ . We have similarly for  $p'$  and  $p''$

$$\log p''/p' = 18.2m (t'' - t')/T'' + \text{small terms} \dots\dots\dots(30)$$

Taking the ratio of these two equations, the small terms are approximately eliminated, the constant goes out, and we obtain the rule already given. Since the logarithms of the tabular pressures  $p'$  and  $p''$  are directly obtained in working the pressures,



there is only one logarithm to look up for each required value of  $t$ . The approximate value of  $T$  required for the final reduction is obtained from that of  $t$  given by logarithmic interpolation in the course of the work, by formula (28). The method is accurate to about a hundredth of a degree over a range of  $10^\circ \text{C.}$ , and is much less trouble in practice than any of the empirical formulae commonly recommended.

In constructing the Steam Tables, the values of  $p$  were first calculated for each  $10^\circ \text{C.}$  from the exact equation (19). Values of  $t$  or  $p$ , at intermediate pressures or temperatures, were then deduced by interpolation. The formula of interpolation employed was somewhat more accurate than the modified rule of logarithmic interpolation previously given, since it was desirable to work the interpolated values to the same order of accuracy as those originally calculated for each  $10^\circ$ . It was devised to take account of the effect of the small terms, and was as follows.

Given  $p', p''$  at  $t', t''$ , to find  $p$  for any intermediate  $t$ ,

$$\log(p/p') = \log(p''/p')(t - t') (1 + (t'' - t)/0.88T) / (t'' - t'). \dots (31)$$

The corresponding formula to find  $t$  for any intermediate  $p$ , is

$$t - t' = (t'' - t') \log(p/p') (1 - (t'' - t)/0.88T'') / \log(p''/p'). \dots (32)$$

These formulae are almost as easy to work in practice as the rule previously given, but have the advantage of being accurate to the required limit over a much greater range. The following example will serve as an illustration of the method of calculation, and a test of the accuracy of the formulae.

Given  $t' = 90^\circ \text{C.}$ ,  $\log p' = 1.00692$ ;  $t'' = 110^\circ$ ,  $\log p'' = 1.81759$ , find  $p$  at  $100^\circ \text{C.}$ ; or conversely, find  $t$  when  $p = 14.689$ , or  $\log p = 1.16699$ . We have

$$\log(p''/p') = .81067. \quad (t - t') / (t'' - t') = 10/20.$$

$$\text{Half } \log(p''/p') = .155385$$

Also

$$0.88T = 328.$$

Add  $10/328$  of  $.155385$  (worked on a slide-rule)

$$= .00474$$

$$\text{sum} = \underline{\underline{.16007}}$$

The sum of these two terms gives  $\log(p/p')$  correct to the last figure. The correction term  $.00474$  represents the error of simple logarithmic interpolation, which in this case amounts to about 1.1 per cent. on the value of  $p$ , whereas the rule given is about 300 times as accurate over a range of  $20^\circ$ .

To find  $t$  for any given  $p$  is not quite so easy because this

involves the ratio  $\log(p/p')/\log(p''/p')$  (or  $\cdot 16007/\cdot 31067$  in the present example) which when multiplied by  $(t'' - t')$  gives  $10\cdot 805^\circ$ , the first approximation to  $(t - t')$  by logarithmic interpolation. This must be reduced by  $(t'' - t)/\cdot 88T''$ , or  $10/887$ , of itself, which gives  $- \cdot 805^\circ$ , so that the correct answer is  $(t - t') = 10\cdot 060^\circ$ , or  $t = 100^\circ \text{ C}$ . In practice the first approximation to  $(t - t')$  can be used in finding  $(t'' - t)$  for the small correction, which is then effected by setting the cursor at  $T$  on the slide, and setting the slide back to  $T'' +$  a tenth of  $(t'' - t)$ , without writing down any figures except the differences of the logs of the pressures.

With a table of pressures for each  $10^\circ$  of temperature, the temperature corresponding to any given pressure can be found by this formula correct to  $\cdot 01^\circ$  with the aid of a small slide-rule, or to  $\cdot 001^\circ$  by the aid of a Fuller spiral slide-rule. The chief trouble involved is that of looking up the required logarithms. For this reason the tables of  $p$  and  $V$  for each degree have been constructed, from which any required values can be obtained correct to  $\cdot 01^\circ \text{ C}$ . by simple proportion, without the aid of logarithms. It must be remembered, however, that a change of  $1^\circ$  in the temperature at  $100^\circ \text{ C}$ . makes a difference of nearly 4 per cent. in the pressure, so that results obtained in this way will not be quite so accurate as the tabulated values. It should also be observed that the pressure itself cannot be tabulated with a uniform degree of proportionate accuracy. This property is possessed by the *logarithm* of the pressure, which more nearly represents the actual results of the calculations, and is more often required in numerical work than the pressure itself. For this reason a table of logarithms of the pressure is also given for each degree, which will give more exact results by interpolation, and is also more useful in finding the entropy or working out expansion curves.

The corresponding table of volumes of saturated steam for each degree, has been calculated directly from the logarithms of the pressures by means of the characteristic equation

$$V = RT/ap + b - c.$$

In using this table for adiabatic expansion, it must be remembered that the quantity which occurs in the adiabatic equation

$$P^n (V - b)^{n+1} = \text{constant},$$

is not  $V$  but  $V - b$ , which makes an appreciable difference when the pressure is high and the volume small. For most practical purposes, the quantity  $b$  might have been omitted altogether from

the equations, but it has been retained on account of its theoretical significance, and cannot be neglected in the calculations without introducing small numerical inconsistencies.

## 72. Empirical Formula for the Saturation Volume.

A formula for the saturation volume of the type  $pV^m = \text{constant}$ , was given by Rankine with the value  $m = 17/16$  for the index deduced by means of Clapeyron's equation from Regnault's formulae for the total heats  $H$  and  $h$  and the saturation pressure. With the new values of the total heat, deduced from the throttling experiments and the specific heat, a formula of the same type still holds very closely, but the value of the index must be changed to  $m = 16/15$ , as deduced by Mollier from the author's equations. The value of the constant is 490, when the pressure is in pounds per sq. in. and the volume in cu. ft. per lb., or 1.786 for kg. per sq. cm. and cu. m. per kg. But in practice it is generally necessary to employ the equation in the logarithmic form

$$\log_{10} V_s = 2.5222 - 15 (\log_{10} p)/16 \text{ (F.P.C. or F.)} \dots(83)$$

The order of agreement between this empirical formula and the values deduced from the characteristic equation, is shown in the following table.

Table II.

Temp. Cent.	Volume of saturated steam in cubic feet per pound	
	By empirical formula	By characteristic equation
0°	3270	3276
50°	192.0	192.7
100°	26.79	26.79
150°	6.270	6.280
200°	2.072	2.074
250°	0.874	0.870

The excellence of the agreement over so wide a range is due to the fact that, although the index  $m$  is really a variable, it passes through a maximum slightly greater than 16/15 in the neighbourhood of 120° C. The mean value of  $m$  over any desired range such as  $p'$  to  $p''$  is given by the formula

$$m = \log (p'/p'')/\log (V''/V'), \dots\dots\dots(84)$$

where  $V'$ ,  $V''$  are the dry-saturated volumes at  $p'$ ,  $p''$ . The value

of  $m$  at any particular point of the saturation curve may be deduced from the expression

$$\begin{aligned} m &= -V(dp/dV)/p \\ &= (1-D)/(1-Sp \times (dT/dp)/S_0T), \dots (85) \end{aligned}$$

where  $D$  is the deviation ratio  $a(c-b)p/RT$ . The limiting value at low pressures when  $D=0$ , and  $S=S_0$ , is the reciprocal of  $1-p(dT/dp)/T$ , which has the value 1.053 at  $0^\circ\text{C}$ ., and evidently cannot be constant. The value of  $m$  reaches a maximum of about 1.069, and falls again at high pressures owing to the increase of  $D$ .

**73. Empirical Formula for  $p$  from  $200^\circ$  to  $374^\circ\text{C}$ .**  
It has become the custom of recent years to endeavour to represent the saturation pressure all the way from  $0^\circ\text{C}$ . up to the critical point by elaborate empirical formulae extending to high powers of the temperature. There is no particular difficulty in representing any selected set of observations as closely as may be desired by a formula of this type. But the result is of no theoretical value, and of little practical utility, because pressures exceeding 250 lbs./sq. in. are seldom used except in small automobile engines, where accurate tests are impracticable, and other considerations are more important than

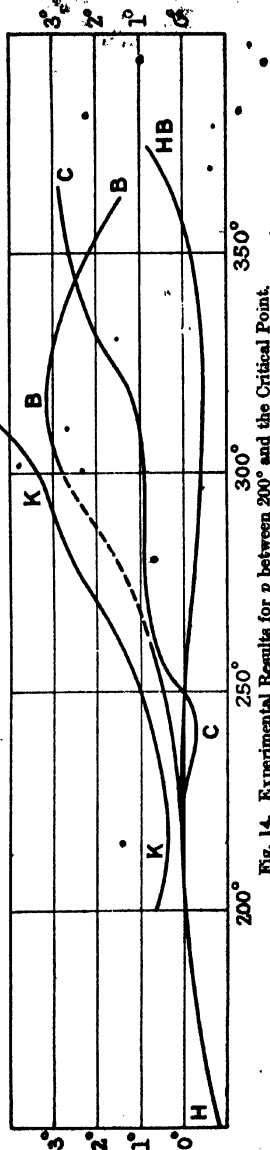


Fig. 14. Experimental Results for  $p$  between  $200^\circ$  and the Critical Point.

efficiency. Owing to the uncertainty of the experimental results, it is desirable to employ the simplest possible type of formula for purely speculative purposes in the neighbourhood of the critical point. There is a considerable amount of evidence, derived from the behaviour of other vapours, that a formula of the simple type  $\log(p/p_0) = K/T_0 - K/T$ , though certainly inadequate at low pressures, represents the saturation curve with remarkable fidelity at high pressures over a considerable range. A suitable formula of this type in the case of steam is as follows:

$$\log p = 2.85265 + 4.264(t - 200)/T \text{ (F.P.C.)}, \dots(86)$$

in which the constants are chosen to give the same values as the theoretical equation for both  $p$  and  $dp/dt$  at  $200^\circ \text{C.}$ , so that the curve joins continuously with the theoretical curve at this point. The formula has the advantage of giving the simple expression  $4645/T$  for the ratio  $(T/p)(dp/dt)$ , and agrees sufficiently well with experiment for practical purposes, as indicated by the annexed figure.

The zero line in the figure represents the empirical formula (86). The curves represent the smoothed results of various series of experiments. The difference of each experimental result from the formula is expressed in degrees of temperature as previously explained. The curve CC represents the observations of Caulet and Colardeau (*Journ. Phys.*, 1891); the curve BB those of Battelli (*Ann. Chim. Phys.*, 1892-94); the curve KK those of Knipp (*Phys. Rev.*, 1900). All of these give much higher results for  $p$  than formula (86). But the curve HB, representing the latest results of Holborn and Baumann (*Ann. Phys.*, 1910), which are probably the most accurate, gives slightly lower results than the formula between  $250^\circ$  and  $360^\circ \text{C.}$  It is very likely that the values of  $p$  given by the formula may be too high in this region, but the difference shown does not greatly, if at all, exceed the probable errors of experiment.

## CHAPTER VIII

### THE CRITICAL STATE

74. **Properties of  $\text{CO}_2$ .** It would be beyond the scope of the present work to attempt a review of all the various speculations current with regard to the critical state, or to construct a system of equations capable of representing the properties of steam consistently in this region, but some reference is necessary in order to prevent misapprehensions, and a general account of the phenomena may be of interest as illustrating the difficulties to be encountered in framing a complete theory. The critical temperature and pressure in the case of steam are so high that there are grave experimental difficulties in the measurement of any of the other physical properties of the fluid in this region, and there is little prospect of being able to utilise them efficiently in any kind of engine. On the other hand, the substance  $\text{CO}_2$ , commonly known as carbonic acid, is often employed for refrigerating purposes in the neighbourhood of its critical point, and its properties in this region have been most carefully investigated by many skilful experimentalists. For this reason, illustrations of critical phenomena will be taken chiefly from the properties of  $\text{CO}_2$ , for which so many experimental data are available that it is possible to test any theory or formula with reasonable certainty.

*The Critical Temperature* of any substance is readily observed by heating a suitable quantity of the liquid in a sealed tube and observing the temperature at which the meniscus, or surface of separation between the liquid and vapour, disappears. Experiments of this kind were first described by Cagniard de la Tour (*Ann. Chim. Phys.*, 1822-23), who measured the critical temperatures of several liquids in this way. As the temperature is raised, the surface tension of the liquid diminishes, the meniscus flattens out, and finally vanishes when the critical point is reached. The liquid and vapour then mix, and the tube becomes filled with a homogeneous substance. Above the critical point, the liquid cannot be distinguished from the vapour, and no separation into two states can be effected by any increase of pressure. Faraday (*Phil.*

*Trans.*, 1828 and 1845), in his experiments on the liquefaction of gases, came to the conclusion that there was a similar limit of temperature for each gas, above which it could not be liquefied by pressure, but the importance of this point in the liquefaction of gases was not fully realised till a much later date.

*The Critical Pressure.* Cagniard de la Tour made some rough measurements of the pressures at which the meniscus disappeared, but he had no independent means of varying the volume, so that his experiments were necessarily incomplete. The first satisfactory measurements of pressure, temperature, and volume, over a fairly wide range in the neighbourhood of the critical point, were made by Andrews (*Phil. Trans.*, 1869) in the case of  $\text{CO}_2$ . The gas was confined in a calibrated capillary tube over mercury, so that the volume could be varied by means of a screw plunger, and the pressures were simultaneously indicated by a similar capillary containing air. At temperatures below the critical point, the saturation volumes of the liquid and vapour could be estimated from the observed volumes at the beginning and end of condensation, but the pressure in Andrews' experiments did not remain quite constant during condensation at constant temperature owing to a residual impurity, about 1 in 1000, of air. The saturation pressure appeared to vary in a regular manner with temperature following a continuous curve up to the critical point. Above the critical point, no condensation or separation of liquid could be observed, but there were large changes of volume for small changes of pressure, giving rise to well marked points of inflection in the isothermal, which persisted for several degrees above the critical point. The critical temperature was estimated as  $31^\circ \text{C}$ ., and the corresponding pressure as 75 atmospheres, but the air-manometer was not corrected for the deviations from Boyle's law, and the effects of any residual impurity, such as air, on the saturation pressure, tend to increase as the critical point is approached. At a later date, Amagat (*Ann. Chim. Phys.*, 29, p. 186, 1898), employing a similar method with the utmost refinements of accuracy, and paying special attention to the purity of the gas, found the value 72.9 atmospheres for the critical pressure of  $\text{CO}_2$  at a temperature of  $31.85^\circ \text{C}$ ., but owing to the effects of supersaturation and the instability of equilibrium at the critical point, the critical pressure itself is more difficult to determine accurately than the saturation pressure at lower temperatures.

For this reason among others it is advantageous to have an

empirical formula representing all the observations of the saturation pressure as closely as possible. The following formula, which is of the simplest possible type, the same as that employed in the last chapter for steam from 200° C. to the critical point, appears to represent all the best observations for CO<sub>2</sub> within the limits of experimental error:

$$\log_{10} p = 1.5363 + 8.157t/T. \dots\dots\dots(1)$$

The value of the constant 1.5363 in the above formula gives the saturation pressures in atmospheres of 760 mm. (lat. 45°), in terms of which most of the observers have expressed their results. If the pressure is required in lbs. per sq. in. (London), the value of the constant is 2.7033. The temperature  $t$  is to be reckoned from the freezing point of water. The corresponding formula for the ratio  $L/ap (V - v)$ , or  $(T/p) dp/dt$ , is  $1985/T$  Cent., or  $3573/T$  Fahr.

The following table shows a comparison of this formula with the results of observation which appear to be most reliable:

Table I.

Saturation pressures of liquid CO<sub>2</sub> in atmospheres of 760 mm.

Temp. Cent.	-50°	-40°	-30°	-20°	-10°	0°	+10°	+20°	+30°
Amagat, 1893	—	—	—	—	—	34.3	44.2	56.3	70.7
and R., 1902	6.60	9.82	14.0	19.3	26.0	34.34	—	—	—
and S., 1906	6.72	9.88	14.1	19.5	25.8	—	—	—	—
and P., 1914	6.66	9.86	14.0	19.3	26.0	34.6	44.7	56.8	—
Formula (1)	6.74	9.88	14.02	19.36	26.08	34.38	44.43	56.45	70.60

References: Amagat, *Annales de Chimie et Physique*, Vol. 29, p. 136, 1893.

K. and R. Kuenen and Robson, *Phil. Mag.*, Vol. 3, p. 154, 1902.

Z. and S. Zeleny and Smith, *Phys. Zeit.*, Vol. 7, p. 667, 1906.

J. and P. Jenkin and Pye, *Phil. Trans. A*, Vol. 213, p. 67, 1914.

The observations of Regnault (utilised by Mollier) are not included in the table, as they are much higher than any of the others, and he did not consider them satisfactory himself. The values which he gives at temperatures above the critical point cannot represent true equilibrium. Jenkin and Pye consider that their values are probably a little too high owing to a small impurity of air. The liquid curve can be followed 5° or 10° below the freezing point, which is at -56.2° C. and 5.2 atmospheres.

*The Critical Volume.* Accurate measurements of the saturation volumes of liquid and vapour in the neighbourhood of the critical point become very difficult owing to the rapid changes with pressure



and temperature. The critical volume itself cannot be measured directly, because the isothermal compressibility  $(1/v)(dv/dp)_t$ , becomes infinite of the second order at the critical point. The usual method in such a case is to measure corresponding values of  $V$  and  $v$  under saturation pressure at a series of temperatures approaching the critical point as closely as possible, and to estimate the critical volume itself from the limiting value of the mean of  $V$  and  $v$ . Cailletet and Mathias (*Journ. de Phys.*, II, Vol. 5, p. 549, 1886), found that better results could be obtained by taking the mean of the densities  $1/V$  and  $1/v$ , which gave a more symmetrical curve than the volumes. The diameter of the curve obtained by plotting the mean of the densities of the liquid and vapour, as in the following figure, turns out to be nearly rectilinear in the case of  $\text{CO}_2$  over a wide range of temperature, and can be produced to the critical point with some degree of confidence, assuming that it presents no singularities beyond the limits of experimental measurement of  $V$  and  $v$ . Cailletet and Mathias measured the saturation volume of the vapour  $V$  at each temperature by observing the disappearance of the last drop of liquid in a capillary tube when the volume was gradually increased at constant temperature. This tends to give too small a result for  $V$ , or too large a result for  $1/V$ , owing to surface condensation, because the ratio of surface to volume is rather high in a capillary tube. They measured the difference of the densities of the liquid and vapour by a hydrostatic method in terms of the density of mercury, and deduced the density of the liquid by adding that of the vapour previously measured. For some reason, the values they obtained for the density of the liquid are appreciably lower than those subsequently observed by Amagat, employing the more direct method of measuring the volume in a calibrated tube. The coefficient of expansion of liquid  $\text{CO}_2$  is very high, being equal to that of a gas at  $-25^\circ \text{C.}$ , where the cooling-effect vanishes, and increasing more and more rapidly up to the critical point, where it becomes infinite.

The smooth curve in Fig. 15 represents Amagat's table of results (*loc. cit.*, p. 186), obtained by producing the observed isothermals for liquid and vapour on the  $PV$ ,  $P$  diagram to the saturation pressure at each temperature. This method has the advantage of eliminating much of the error due to surface condensation, since the result does not depend exclusively on the observations at the saturation point. But the isothermals are so steep near the critical

point that it is difficult to perform the extrapolation satisfactorily, and the behaviour of other substances would appear to indicate that the curves of liquid and vapour are not so exactly symmetrical as is shown by Amagat's table for  $\text{CO}_2$ . The observations of Cailletet and Mathias, indicated by the (x) crosses, differ systematically from those of Amagat, but give nearly the same diameter. Their observations of the density of the liquid do not extend beyond  $22.2^\circ \text{C}$ . Those of Behn (*Ann. Phys.*, 3, p. 788, 1900), indicated by the (+) crosses, were made by a delicate hydrometer method, and are very consistent. They extend down to  $-60^\circ \text{C}$ ., but do not go above  $24.8^\circ \text{C}$ . They overlap Amagat's observations from  $0^\circ$  to

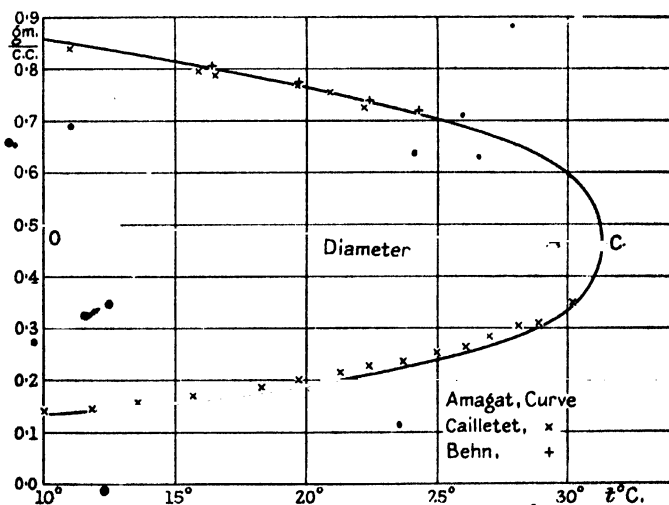


Fig. 15. Rectilinear Diameter of density curve for  $\text{CO}_2$ .

$25^\circ \text{C}$ . When combined with Amagat's vapour-densities, they give a diameter OC, which is an exact straight line within the limits of experimental error, giving for the mean of the densities in gm./c.c., the simple equation

$$(1/V + 1/v)/2 = 0.5125 - 0.00148t. \dots\dots\dots(2)$$

The extrapolation of this diameter to the critical point gives the critical density  $0.465 \text{ gm./c.c.}$  In the case of many other substances the diameter of the curve representing the saturation densities of liquid and vapour is appreciably curved, and there is no theoretical reason why it should not present singularities near the critical point.

But there is no experimental evidence that the diameter is otherwise than straight in the case of  $\text{CO}_2$ , and the simple equation (2), when taken in conjunction with a formula for the latent heat  $L$ , giving the difference  $V - v$  from Clapeyron's equation, affords an independent method of deducing consistent values of the saturation volumes of both liquid and vapour in the region near the critical point where the direct experimental evidence is somewhat deficient and uncertain. Values of  $V$  and  $v$  obtained from  $L$  in this way are in close agreement with Amagat's when the same value of  $L$  at  $0^\circ \text{C.}$  is assumed.

*The Latent Heat.* The values of  $p$ ,  $1/V$ , and  $1/v$ , in Amagat's table, give all the necessary data for calculating the values of  $L$  from  $0^\circ$  to  $80^\circ \text{C.}$ , by means of Clapeyron's equation, but it is best to utilise formula (1), which gives  $1985p/T$  for the factor  $Tdp/dt$ . Below  $0^\circ \text{C.}$ , the direct observations of  $L$  by Jenkin and Pye (*loc. cit.*) are the only experimental data available, and are represented very closely from  $-50^\circ$  to  $+20^\circ \text{C.}$ , by a formula of the Thiesen type, as follows:

$$\log_{10} L = 1.1164 + 0.4115 \log_{10} (81.5 - t), \dots\dots\dots(8)$$

in which the critical temperature is taken as  $81.5^\circ \text{C.}$

The following table shows a comparison of the experimental values with those given by the above formula.

Table II.  
Latent heat of vaporisation of liquid  $\text{CO}_2$  in cals. C.

Temp. Cent.	$-50^\circ$	$-40^\circ$	$-30^\circ$	$-20^\circ$	$-10^\circ$	$0^\circ$	$+10^\circ$	$+20^\circ$	$+30^\circ$	$31^\circ$
Amagat	—	—	—	—	—	56.1	47.7	36.5	14.8	7.80
J. and P.	79.9	75.7	71.3	66.5	60.9	54.1	46.2	36.55	—	—
Formula (3)	80.0	75.8	71.2	66.2	60.6	54.1	46.2	35.7	15.4	9.97

There is a discrepancy of nearly 2 cals. C. between the values of  $L$  deduced from  $V$  and those given by Jenkin and Pye at  $0^\circ$  and  $10^\circ \text{C.}$  Almost any equation that can be employed to give values of  $V$  consistent with Amagat's value at  $0^\circ \text{C.}$  and with the curve of saturation pressure, will give values of  $L$  higher than (8) by a nearly constant difference of 2 cals. C. from  $0^\circ$  to  $-50^\circ \text{C.}$  This is not without significance, because the values of  $V$  are more likely to be correct at low pressures than those of  $L$ , which are extremely difficult to measure, and are generally liable to err in defect. The observed values of  $V$  at high pressures are also liable

to err in defect, so that it would not be surprising if the values of  $L$  given by (8) should prove eventually to be systematically too low. It is probable that a formula of this type would give more satisfactory values of  $L$  near the critical point than could be deduced from observations of  $V$  and  $v$ , if the critical temperature were known with certainty. The difference between the value  $31.5^\circ$  assumed in (8) and Amagat's value  $31.35^\circ$  C. is almost sufficient to account for the differences shown in the table at  $30^\circ$  and  $31^\circ$  C., but it is just as likely that there are systematic errors in  $V$ .

The continuous curve in Fig. 16 represents the empirical formula (8) for the latent heat. The dots represent the observations of Jenkin and Pye extending from  $-53^\circ$  to  $+20^\circ$  C. The broken

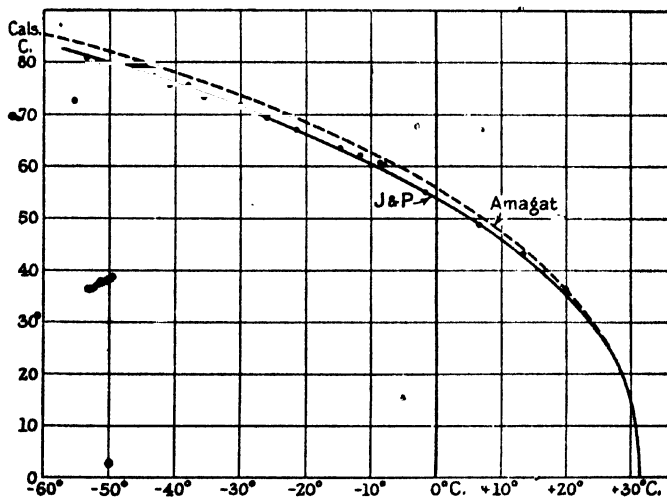


Fig. 16. Latent Heat of  $\text{CO}_2$  in cal. C.

curve from  $0^\circ$  C. to the critical point represents values of  $L$  calculated from Amagat's table of  $p$ ,  $V$ , and  $v$ . The continuation of this curve down to  $-60^\circ$  C. represents the values of  $L$  obtained by combining equation (39) for  $V$  with the observed values of  $v$ , and deducing the equation of saturation-volume (48) from the values of  $h$  represented by equation (4) of the next section, as explained later.

The broken curve in Fig. 16, can be equally well fitted with a formula of the Thiesen type, namely,

$$\log_{10} L = 1.1468 + 0.4018 \log_{10} (31.5 - t), \dots\dots(8b)$$

which would agree very closely with Amagat's table up to the critical point if the critical temperature were taken as  $81.85^{\circ}\text{C}$ . But any small disagreement near the critical point would be of little significance, because the actual values of  $V$  and  $v$  cannot be observed satisfactorily in this region. The critical temperature is taken as  $81.5^{\circ}\text{C}$ . in both formulae for the sake of uniformity. The exact value is necessarily a little uncertain owing to the effect of impurities, which were not completely eliminated even in the observations of Amagat, and which tend to depress the observed value of the critical temperature and to raise that of the critical pressure in this particular case.

*The Total Heat.* The total heat is the most important quantity for thermodynamical purposes. In order to complete the solution for saturated  $\text{CO}_2$ , and to obtain consistent values of  $H$  in the neighbourhood of the critical point, it is necessary to assume a formula either for  $H$  or  $h$ , consistent with the critical conditions and with the experimental values at lower temperatures. The simplest way to do this is to adopt a formula of the same type as that already applied in the case of water, Chapter II (5), namely,

$$H - aVTdp/dt = h - avTdp/dt = TdG/dT - G = 0.42t - 6.53, \quad (4)$$

which has the advantage of giving simple and exact expressions for the entropy of the liquid and vapour, and of being consistent with the condition that both  $dH/dT$  and  $dh/dt$  become infinite, but with opposite signs, at the critical point. The value of the constant 0.42, like the corresponding constant in the case of water, is a little greater than twice the value of the specific heat of the vapour at zero pressure, which is 0.208 in the case of  $\text{CO}_2$  at its critical temperature. The formula is equivalent to assuming that the coefficient  $Td^2G/dT^2$  remains finite and equal to 0.42. There is no thermodynamical reason why this coefficient should necessarily be constant, but the constant value selected appears to satisfy the experimental data within the limits of probable error, as is shown in the following table.

Table III. Total heat  $h$  of liquid  $\text{CO}_2$  in cal. C.

Temp. Cent.	-50°	-40°	-30°	-20°	-10°	0°	+10°	+20°
J. and P. (1914)	-27.3	-22.1	-16.8	-11.4	-5.8	0	+6.35	+12.55
Formula (4)	-26.27	-21.51	-16.55	-11.37	-5.88	0	+6.45	+12.55

There appeared at first to be a systematic divergence below  $-20^{\circ}\text{C.}$  between the values calculated by (4) and those tabulated by Jenkin and Pye in their first paper (1914). The observations subsequently given in their later paper (*Phil. Trans.*, A, 215, p. 360, 1915) appear to differ from (4) by a few tenths of a calorie only in the *opposite* direction, but it is not possible to give exact figures as they do not give a corrected table of  $h$ . The discrepancy in their experimental value at  $+20^{\circ}\text{C.}$  rests on a single observation of the mean specific heat of the liquid at 900 lbs. from  $-12^{\circ}$  to  $+19.2^{\circ}\text{C.}$ , and the observed increase of  $h$  from  $10^{\circ}$  to  $20^{\circ}$  according to their table is *less* than that from  $0^{\circ}$  to  $10^{\circ}$ , which is clearly impossible, since the rate of increase of  $h$  becomes infinite at the critical point. They found in fact that "the liquid limit curve between  $10^{\circ}$  and  $28^{\circ}$  did not fit quite satisfactorily" in their  $H\Phi$  diagram. The values of  $h$  and  $\phi$  shown on their diagram at the critical point itself agree, as nearly as they can be estimated, with those given by equation (4), with Amagat's value of  $v$  at the critical point. The constant 6.58 in equation (4) is the value of the term  $avTd\phi/dt$  at  $0^{\circ}\text{C.}$ , so that  $h = 0$  at  $0^{\circ}\text{C.}$ , according to the usual convention. Jenkin and Pye take  $h = apv = +0.91$  cal. at  $0^{\circ}\text{C.}$  in their table. The constant 0.9 has accordingly been subtracted from their values of  $h$ , as given in Table III above, for comparison with the formula (4).

*Empirical Table for the Properties of  $\text{CO}_2$  at Saturation.* The values given in the following table have been calculated from equations (1), (2), (3), and (4), without direct reference to Amagat's table, for the sake of uniformity and consistency, because Amagat's table does not extend below  $0^{\circ}\text{C.}$  It is quite likely that Amagat's value, 0.166 for  $V_c$  at  $0^{\circ}\text{C.}$ , in F.P.C. units, is more nearly correct than the value 0.1605 given in the table, as deduced from equation (8) for  $L$ . This could easily be represented, if desired, by taking the second formula (8 b) with  $L = 56$  at  $0^{\circ}\text{C.}$ , and 82 at  $-50^{\circ}\text{C.}$

It is theoretically probable that the values of  $p$  given by (1) are a little too high below  $-80^{\circ}\text{C.}$ , and that the corresponding values of  $dp/dt$  and  $V$  are uncertain in this region. Such points could not be settled satisfactorily without more exact knowledge than we at present possess of the theory of the critical state and the form of the characteristic equation, without which it is impossible to construct a completely consistent system of equations, including the field of the liquid and the superheated vapour in addition to the saturated state. This extension is full of difficulties, which will be illustrated in later sections. In the meantime it is better to have

an exact system of equations summarising the experimental data for the saturated state, than a set of tables by different experimentalists which are necessarily more or less discontinuous and inconsistent.

Table IV.

\*Properties of saturated carbonic acid in F.P.C. units.

$t$	$p$	$100v$	$100V_L$	$L$	$h$	$H$	$\phi$	$\Phi$
- 50°	99.0	1.386	89.67	80.00	- 26.27	+ 53.73	- 0.1032	0.2554
- 45°	120.4	1.409	73.73	77.91	- 23.91	+ 54.00	- 0.0929	0.2487
- 40°	145.1	1.433	61.06	75.77	- 21.51	+ 54.26	- 0.0826	0.2424
- 35°	173.5	1.459	50.89	73.54	- 19.06	+ 54.48	- 0.0724	0.2365
- 30°	206.0	1.488	42.65	71.20	- 16.55	+ 54.65	- 0.0622	0.2307
- 25°	242.8	1.519	35.94	68.77	- 13.99	+ 54.78	- 0.0521	0.2251
- 20°	284.4	1.552	30.42	66.21	- 11.37	+ 54.84	- 0.0418	0.2198
- 15°	331.0	1.589	25.84	63.47	- 8.67	+ 54.80	- 0.0315	0.2144
- 10°	383.1	1.631	22.00	60.55	- 5.88	+ 54.67	- 0.0212	0.2090
- 5°	441.0	1.678	18.79	57.45	- 3.00	+ 54.45	- 0.0107	0.2036
0°	505.0	1.731	16.05	54.06	0	+ 54.06	0	0.1980
+ 5°	575.6	1.795	13.72	50.36	+ 3.15	+ 53.51	+ 0.0110	0.1921
10°	652.8	1.866	11.68	46.21	6.45	52.66	0.0222	0.1854
15°	737.4	1.957	9.889	41.44	9.99	51.43	0.0340	0.1778
20°	829.3	2.075	8.258	35.71	13.85	49.56	0.0467	0.1685
25°	929.2	2.250	6.688	28.24	18.29	46.53	0.0609	0.1556
30°	1037	2.641	4.854	15.45	24.52	39.97	0.0807	0.1317
31.5°	1071	3.438	3.438	0	31.38	31.38	0.1030	0.1030

Formulae for the above quantities:

Saturation pressure,	$\log_{10} p = 2.7033 + 3.157 t/T$ .....	(p)
Rectilinear diameter,	$1/v + 1/V = 64 - 0.185t$ .....	(v)
Clapeyron's equation,	$ap(V - v) = Lp/T (dp/dt) = LT/1985$ .....	(V)
Latent heat (Thiessen),	$\log_{10} L = 1.1164 + 0.4115 \log_{10} (31.5 - t)$ .....	(L)
Total heat of liquid,	$h = 0.42t + vL/(V - v) - 6.53$ .....	(h)
Total heat of vapour,	$H = 0.42t + VL/(V - v) - 6.53$ .....	(H)
Entropy of liquid,	$\phi = 0.42 \log_e T/273 + vL/T(V - v) - 6.53/273$ ....	(φ)
Entropy of vapour,	$\Phi = 0.42 \log_e T/273 + VL/T(V - v) - 6.53/273$ ....	(Φ)

These equations are of the same type as those employed for steam in the similar Table X at the end of this chapter.

**The Specific Heat of CO<sub>2</sub>.** The properties of the liquid and vapour in the saturated state are the most important for refrigeration purposes, and it is therefore most appropriate to employ the saturation table as the starting point in constructing a diagram. The most useful coefficients in determining the variation of  $H$  outside the saturated region, are the specific heats and the cooling-effect.

The specific heat of the vapour at atmospheric pressure is the easiest to measure, but shows a considerable variation with tem-

perature, which is illustrated by the values at 0° and 100° C. in the following table.

Table V.\* Specific heat of CO<sub>2</sub> at atmospheric pressure.

Observers	Regnault (1862)	E. Wiedemann (1868)	Swann (1910)
at 0° C.	0.1870	0.1952	0.1973
at 100° C.	0.2145	0.2169	0.2213
Increase	0.0275	0.0217	0.0240

Swann (*Phil. Trans. A*, Vol. 210, pp. 199–238, 1910) employed the continuous electric method, which avoids many sources of error, and is best suited for measuring the *variation* of the specific heat. His results when corrected to zero pressure with the aid of the cooling-effect, give the formulae

$$S_0 = 0.1950 + 0.000254t, \quad S_m = 0.1950 + 0.000127t, \dots (5)$$

where  $S_0$  is the specific heat at zero pressure at  $t^\circ$  C., and  $S_m$  is the mean value of  $S_0$  from 0° to  $t^\circ$  C., in mean calories C. These values at zero pressure are useful as a starting point, giving  $H = S_m t + B$  at zero pressure.

Joly (*Phil. Trans. A*, Vol. 182, p. 73, 1891) measured the mean specific heat of CO<sub>2</sub> at constant volume over various ranges of temperature from 10° to 100° C., at high densities, approaching liquefaction. Taking  $L = 536.7$  for steam at 100° C. (Regnault), he gives for the mean specific heat of CO<sub>2</sub> over the whole range 10° to 100° C. at constant volume  $V$ , the formula

$$S_0 = 0.1650 + 0.2135/V + 0.340/V^2, \dots (6)$$

where  $V$  is in c.c./gm. The extrapolation of Joly's values to zero density is a little uncertain, but if we add the constant  $R = 0.0450$  to Joly's value 0.1650, we obtain  $S_0 = 0.2108$  (corrected to  $L = 539.3$ ), which is in fair agreement with Swann's value  $S_0 = 0.2090$  at 55° C., the mean of Joly's range.

*The Cooling-effect C.* Joule and Thomson (*Phil. Trans.*, 1854) measured the cooling-effect for CO<sub>2</sub> at moderate pressures, chiefly in the neighbourhood of 0° and 100° C. Their mean corrected results in F.P.C. units\* may be fairly represented by a curve of the type  $C = KT^{-n}$ , passing through the points

$$C = 0.0944^\circ/\text{lb. at } 0^\circ \text{ C. and } C = 0.0421^\circ/\text{lb. at } 100^\circ \text{ C.,}$$

but if a formula of this type is employed, the required value of the index  $n$  is not 2, as generally quoted, but more nearly 2.66 or 8/3.



Jenkin and Pye (*loc. cit.*, 1915) made some throttling experiments on  $\text{CO}_2$ , from which it is possible to deduce values of  $C$  between  $-80^\circ$  and  $+80^\circ \text{C}$ . These appear to agree very closely with the Joule-Thomson curve, though made at somewhat higher pressures. They tend to confirm the result of Joule and Thomson that  $C$  is nearly-independent of the pressure within moderate limits.

It will be observed on reference to Table IV that the value of  $H$  reaches a maximum for the saturated vapour at a temperature close to  $-20^\circ \text{C}$ . The product  $Cdp/dt$  must equal unity at this point by equation III (7). The value of  $dp/dt$  at  $-20^\circ \text{C}$ . is  $1985p/T^2 = 8.8 \text{ lbs./deg.}$ , by equation (1), the reciprocal of which is  $0.114^\circ/\text{lb.}$ , agreeing almost exactly with the value of  $C$  at the same point from the Joule-Thomson curve.

Assuming that  $C$  is a function of  $T$  only, consistent values of  $H$  and  $S$  at any temperature and pressure within certain limits, are readily obtained from those of  $C$  by the method of Chapter IV, § 89. It is very easy to construct a  $PT$  diagram in this way, since all the lines of constant  $H$  are exactly similar, having the same slope at the same temperature. The values of  $H$  and of  $SC$  for each line are given by the conditions  $H = S_m t_0 + B$ , and  $SC = S_0 C_0$ , where  $C_0, t_0$ , are the values of  $C$  and  $t$  at the point where the line of constant  $H$  meets that of zero pressure. Values of  $H$  and  $S$  found in this way agree very closely with the observations of  $S$  by Jenkin and Pye, and with values of  $H$  obtained by combining Joly's values of  $S_0$  with Amagat's values of  $PV$ . But the method appears to fail somewhat in the neighbourhood of the critical point, where the approach of the liquid state requires a diminution of  $C$  with increase of density. At the critical point,  $Cdp/dt = 1$ , giving  $C = 0.044^\circ/\text{lb.}$ , which is smaller than the value  $0.070$  given by the Joule-Thomson curve at this temperature.

**75. Rankine's Equation for  $\text{CO}_2$ .** In correlating the values of  $H, S$ , and  $C$ , in the neighbourhood of saturation, where they are difficult to measure experimentally, it is desirable to employ expressions consistent with a suitable form of characteristic equation. The majority of equations which have been proposed for representing the deviations of actual gases from the ideal state are founded on that given by Rankine (*Phil. Trans.*, 1854, p. 837), deduced from Regnault's experiments on the compressibility and the pressure-coefficient of  $\text{CO}_2$ , namely,

$$PV/17116 = (t + 274)/274 - A'V_0/V (t + 274). \dots\dots(7)$$

The constant 17116 represents the ideal value of the product  $PV$  in foot-pounds at  $0^\circ \text{C.}$ , where the temperature is taken as  $273^\circ$  on the absolute scale.  $V_0$  is the ideal value of the volume at  $0^\circ \text{C.}$  and 1 atmosphere.  $A'$  is a specific constant, having the value  $1.9^\circ \text{C.}$  for  $\text{CO}_2$ . The drop of temperature  $t_1 - t_2$  in expansion through a porous plug was given by Rankine in the form

$$JS(t_1 - t_2) = 3(P_2V_2 - P_1V_1), \dots\dots\dots(8)$$

where  $V_1$  is the volume at the higher pressure  $P_1$  at a temperature  $t_1$  before passing the plug, and  $V_2$  is the volume at the lower pressure  $P_2$  when the gas has been restored to its original temperature  $t_1$  by supplying heat  $JS(t_1 - t_2)$  at constant pressure  $P_2$  after passing the plug. The product  $P_1V_1$  represents the work done by the pump on the gas per unit mass in forcing it up to the plug. The product  $P_2V_2$  represents the work done per unit mass by the gas escaping at the same temperature. By the first law, the heat which must be supplied to restore the temperature to  $t_1$  is equivalent to the net work, represented by the difference  $P_2V_2 - P_1V_1$ , together with the increase of intrinsic energy  $E_2 - E_1$  in expansion from  $V_1$  to  $V_2$  at constant temperature  $t_1$ . According to equation (7) the increase of  $E$  is exactly twice the increase of  $PV$  at constant temperature, giving the numerical factor 3 in equation (8).

Since Rankine's constant

$$P_0V_0/JT_0 = 17116/1400 \times 274 = 0.0446 \text{ cal./deg.}$$

represents  $R$ , his equation may be put in the more convenient form

$$aP/RT = 1/V - c/V^2, \dots\dots\dots(9)$$

where  $c$  is the coaggregation volume  $c_0(T_0/T)^2$ , and the value of the constant  $c_0$ , according to Rankine, is  $A'V_0/T_0$ , or 0.00693 of  $V_0$ , giving 8.53 c.c. per gm., or 0.0565 cb. ft./lb. The constant  $a$  in the first term of (9) is the usual factor for reducing  $PV$  to cal., according to the system of units employed.

Rankine obtained the expression for the increase of  $E$  in expansion at constant temperature by applying to equation (7) (preferably in the form (9)) the thermodynamical relation given by Kelvin (*Phil. Mag.*, 1852, Vol. iv, p. 170), deduced from the second law of thermodynamics,

$$(dE/dV)_t = aT(dP/dT)_V - aP = 2cRT/V^2, \dots\dots\dots(10)$$

which gives the expression for the intrinsic energy

$$E = s_m t + B' - 2cRT/V, \dots\dots\dots(11)$$

where  $B^*$  is a constant, and  $s_m$  the mean value of the limiting specific heat  $s_0$  at zero density from  $0^\circ$  to  $t^\circ$  C. The corresponding expression for the specific heat  $s$  at any constant volume  $V$  is obtained by differentiation, thus

$$s = (dE/dT)_v = s_0 + 2cR/V. \dots\dots\dots(12)$$

The expressions for  $H$ ,  $S$ , and  $SC$ , are obtained as follows:

$$H = E + aPV = S_mt + B'' - 3cRT/V, \dots\dots\dots(13)$$

$$SC = - (dH/dV)_t / (dP/dV)_t = 3ac/(1 - 2c/V), \dots\dots\dots(14)$$

$$S = (dH/dT)_v + SC (dP/dT)_v = S_0 + 3cR/V + (1 + c/V) RSC/aV, \dots\dots\dots(15)$$

which show that  $SC$  and  $S$  become infinite when  $V = 2c$ . The value of  $C$  at any point defined by  $V$  and  $T$ , is easily found from (14) and (15), thus

$$C = SC/S = 3ac/[S_0(1 - 2c/V) + (2 - c/V)3cR/V]. \dots\dots\dots(16)$$

But the integrated throttle-drop  $t_1 - t_2$  for a finite range, namely,

$$S(t_1 - t_2) = 3c_1RT_1(1/V_1 - 1/V_2), \dots\dots\dots(17)$$

which is Rankine's equation (8) expressed in terms of  $c$ , is troublesome to work, when only  $P_1$  and  $P_2$  are given. The value of  $S$  required is that at  $P_2$  from  $t_1$  to  $t_2$ , which is difficult to calculate unless  $t_2$  is known. Rankine takes  $S = 0.2148$ , Regnault's mean value at atmospheric pressure from  $0^\circ$  to  $200^\circ$  C., which is often quite unsuitable.

The value of  $c_0$  deduced from Rankine's  $A'$  gives fairly good results for  $C$  on the average at moderate pressures, but errs greatly in excess at high pressures near saturation. The limit of  $C$  at zero pressure is  $3ac/S_0$ , and the other limit, when  $V = 2c$ , is  $4ac/3R$ , which is nearly double. The value at  $0^\circ$  C. and  $P = 0$  is 0.090, but that near saturation at  $0^\circ$  C. is 0.128, which is too large, although Rankine's value of  $c$  is too small according to other experimental data which have to be considered. There are more serious objections to Rankine's equation on other grounds at high pressures. It is of interest chiefly as a simple example of a common type.

The order of agreement obtained under working conditions is illustrated by the following numerical example. Jenkin and Pye (*Phil. Trans.*, 1915, p. 380, Table E, Throttling experiment  $T$ ) observed a drop of temperature from  $+13.5$  to  $-15.05^\circ$  C. on throttling from 500 lbs. to 200 lbs. abs. Dividing the drop of temperature by the drop of pressure, we find the mean value  $C = 0.0958^\circ/\text{lb.}$  at 350 lbs. and  $-0.8^\circ$  C., in practically perfect

agreement with the Joule-Thomson curve. On referring to the diagram, Fig. 19, we find that the initial and final states lie on the same horizontal line at  $H = 59$ . To compare the result with Rankine's equation (8) or (17), we have to find the appropriate value of  $S$ , which cannot be done satisfactorily except by calculating  $H$  from (18) at both temperature limits at 200 lbs., and dividing the difference by the difference of temperature. The equation then reduces identically to  $H' = H''$ , showing that the calculation of  $H$  at  $18.5^\circ \text{C}$ . and 200 lbs. was superfluous, and that it would save trouble to write the equation directly in the form

$$S_m(t' - t'') = 3c'RT'/V' - 3c''RT''/V'', \dots\dots(18)$$

where  $S_m$  is known, being the mean value of  $S_0$  from  $t'$  to  $t''$ , namely  $0.1949$  in the present case, giving  $t' - t'' = 33.9^\circ$ , or  $t'' = -20.4^\circ \text{C}$ ., showing that Rankine's equation gives too large a value of  $C$  near saturation.

The most direct method of performing the verification, is to calculate the values of  $H - B$  from (13) at each limit, and find  $t''$  by interpolation, thus:

At  $P = 500$ ,  $t = +13.5^\circ$ :  $S_m = 0.1967$ ,  $c = 0.0513$ ,  $V = 0.1795$ ,  $H - B = -8.430$ .

At  $P = 200$ ,  $t = -15.1^\circ$ :  $S_m = 0.1931$ ,  $c = 0.0633$ ,  $V = 0.4930$ ,  $H - B = -7.388$ .

At  $P = 200$ ,  $t = -20^\circ$ :  $S_m = 0.1925$ ,  $c = 0.0658$ ,  $V = 0.4800$ ,  $H - B = -8.544$ .

By interpolation at 200 lbs.,  $H' = H''$ , when  $t'' = -19.5^\circ \text{C}$ . The most difficult part of the calculation with an equation of this type, giving  $H$  in terms of  $V$  instead of  $P$ , is to find  $V$  in each case from (9).

Rankine's equation (12) makes  $s$  a linear function of the density at constant temperature. Joly found this to be the case provided that the temperature range did not extend below the critical point, below which a quadratic function of the density was required as shown in equation (6). Joly's observations afford an independent method of calculating  $c$  in Rankine's equation. Since Joly's  $S_0$  represents the mean rate of increase of  $E$  per degree over a considerable range of  $t$ , the comparison is best effected by reference to equation (11) for  $E$ , which gives, on substituting  $c = c_0(T_0/T)^2$ , a simple equation for  $c_0$

$$S_0 = (E' - E'')/(t' - t'') = s_m + 2Rc_0T_0^2/VT'T''. \dots(19)$$

Taking Joly's first formula,  $S_0 = 0.1657 + 0.2064/V$ , applying to moderate densities, we find  $c_0 = 8.25 \text{ c.c./gm.}$ , slightly less than Rankine's value. But if we take his later formula (6), applying to a

mean volume 7.62 c.c./gm. we find an average value  $c_0 = 4.06$  c.c./gm., or 0.0650 cb. ft./lb., which is considerably larger. The method is not very satisfactory for finding  $c$ , because the change of  $S_0$  with density over the experimental range is relatively small, being only about 12 per cent. of the whole quantity measured, and because the quadratic formula (8) does not exactly correspond with Rankine's equation (11) for  $E$ .

Joly also endeavoured to obtain evidence of the variation of  $S_0$  with temperature by making experiments over different ranges of temperature, but was unable to detect any change with certainty. This has been quoted as casting doubt on Swann's equation (5) for the variation of  $S_0$  with temperature, which ought to be the same as that of  $s_0$ . The apparent discrepancy is explained by reference to equation (19). The value of  $s_m$  will increase as the range of temperature is raised, but that of the second term will diminish with increase of the limits  $T'$  and  $T''$ . If Swann's value is taken for the rate of increase of  $s_m$ , it happens that, for the densities chiefly employed by Joly in this investigation, the rates of change of the two terms are nearly equal and of opposite sign for a mean temperature in the neighbourhood of  $50^\circ \text{C}$ .

A similar effect occurs in the variation of the specific heat at constant pressure with temperature according to equation (15), but at much lower pressures, because the variation of  $S$  with pressure is much greater than that of  $s$ . When the increase of  $S_0$  with rise of temperature is compensated by the diminution of  $c$  and  $1/V$ , there will be a minimum value of  $S$  at each constant pressure, accompanied by a slow rate of variation over a considerable range of temperature. According to (15) the minimum for  $S$  at 150 lbs. should occur in the neighbourhood of  $0^\circ \text{C}$ ., which explains the fact that Jenkin and Pye were unable to detect with certainty any variation in the value of  $S$  at this pressure, from  $-30^\circ$  to  $+30^\circ \text{C}$ .

As explained by the author (*Phil. Mag.*, Jan. 1908), the agreement of Rankine's equation with observations of the specific heat, cooling-effect, and compressibility, is greatly improved, even at moderate pressures, by the introduction of the covolume  $b$ , as proposed by Natterer (*Wiener Ber.*, 1850-54), and further developed by Hirn (*Théorie Méc. de la Chaleur*, vol. 2, p. 211), to represent the limit of compressibility at high pressures. Some modification of this kind is obviously necessary, because Rankine's equation, in its original form (7) or (9), gives maximum values of  $P$  when

$V = 2c$ , and imaginary values of  $V$  when  $P$  exceeds  $\frac{a}{4c}$ . The simplest way of removing these difficulties is to put  $V = b$  for  $V$  in the first term of (9), which then becomes

$$aP/RT = 1/(V - b) - c/V^2 \dots \dots \dots (20)$$

This simple addition makes no change in the expressions for  $E$  and  $S_0$  if  $b$  is regarded as constant, but the equations for  $H$ ,  $S$ , and  $SC$ , become

$$H = S_m t + B - 8cRT/V + bRT/(V - b), \dots \dots \dots (21)$$

$$SC = a [3c - bV^2/(V - b)^2] / [V^2/(V - b)^2 - 2c/V], \dots \dots (22)$$

$$S = S_0 + 8cR/V + bR/(V - b) + (R/(V - b) + cR/V^2) SC/a, \dots (23)$$

If the critical pressure is taken as  $P_c = 1071$  lbs. at  $t_c = 81.5^\circ \text{C.}$ , with  $R = 0.0451$  cal. deg. C., we find

$$c_0 = 0.0655, \quad b = 0.0156 \text{ cb. ft./lb.}$$

With these expressions, the anomalies in the values of  $C$  at high pressures disappear. Thus the value of  $C$  at  $30^\circ$  and 1037 lbs. is less than  $C_0$  at  $30^\circ$  and zero pressure, instead of greater, but  $C$  at 500 lbs. is nearly equal to  $C_0$ , confirming the experimental results at these pressures. Values of  $S$  calculated from (23) give good agreement with the observations of Jenkin and Pye over the whole experimental range as shown in the following table.

Table VI.

$S$  Observed by J. and P., compared with  $S$  Calculated by (23).

Pressure	150 lbs.	200 lbs.	300 lbs.	400 lbs.	500 lbs.	700 lbs.
Temp. C.	Obs. Calc.	Obs. Calc.	Obs. Calc.	Obs. Calc.	Obs. Calc.	Obs. Calc.
- 30°	2345 2301	270 253	— —	— —	— —	— —
- 15°	2315 2246	258 240	292 287	— —	— —	— —
0°	2315 2216	246 234	277 264	330 313	396 404	— —
+ 15°	2315 2209	234 230	261 252	296 282	347 326	547 572
+ 30°	2315 2210	221 228	246 245	263 266	298 294	378 386

NOTE. To save space, the decimal point is omitted before each value of  $S$ .

The values of  $S$  tabulated by Jenkin and Pye were required in the construction of their  $H\Phi$  diagram by a step-by-step process, and were obtained by drawing tangents to the curves representing their observations on the variation of  $H$ . Formula (23), though deduced from totally independent data, fits the observations as closely as if it had been specially calculated from the observations themselves, and affords strong confirmation of the accuracy and

consistency of the experiments. The small discrepancies shown in the table would have very little effect on the values of  $H$ , and may fairly be attributed to accidental errors. It is hardly possible, for instance, that the value of  $S$  at  $30^\circ \text{C.}$  should be *less* at 200 lbs. than at 150 lbs., as shown by the observed values 0.221 and 0.2318.

The agreement of the values of  $C$  deduced from (22) and (23) with those found by Joule and Thomson and by Jenkin and Pye, is equally good over the experimental range, but is less important, because the range of variation of  $C$  is much less than that of  $S$ . It follows that the expression (21) must represent the variation of  $H$  correctly according to the same experiments, provided that the appropriate value of  $V$  is calculated from (20) for the given values of  $P$  and  $T$  at each required point. The expressions for  $S$  and  $C$  are not required in calculating  $H$ , but are useful as an auxiliary means of verifying experimental data. The values of  $H$  at saturation can be fitted very approximately with those already given in Table IV by using the appropriate value of the constant  $B$  in (21), but it by no means follows that the values of  $V$  given by (20) with those of  $p$  taken from (1) will fit with the values of  $V$ , in Table IV calculated from  $L$  and  $dp/dt$  by Clapeyron's equation. As a matter of fact the values of  $V$  from (1) and (20) differ from those given in Table IV in the same direction as Amagat's, but slightly more, indicating that the values of  $L$  given by (8) are systematically ~~too~~ low, or that there is a systematic error in the formula for  $p$ . An exact fit could be obtained only by finding the equation of saturation pressure consistent with (20). This is a highly debatable problem, which has given rise to endless discussion. It will be instructive to consider some of the difficulties, though no completely satisfactory solution has yet been obtained owing to the complexity of the conditions to be satisfied.

**76. The Continuity of State.** In the ordinary process of evaporation or ebullition at constant temperature and pressure, the change of state from liquid to vapour takes place only at the surface of separation, and is a discontinuous process in the sense that all parts of the substance are not simultaneously affected. The state of the substance at any stage of the transformation is not homogeneous, but consists of two separate parts liquid and vapour, in equilibrium at the same temperature and pressure. The change is represented on the indicator diagram in the annexed figure (17), which is drawn nearly to scale for  $\text{CO}_2$ , by the horizontal line DEF

at 45 atmospheres, which is the saturation pressure at  $10^{\circ}\text{C}$ . Any point of the line, such as E, represents a mixture of liquid and vapour in the ratio of EF to DE by weight. The point F represents the state of dry saturated vapour, D that of complete condensation to liquid. The curve DL represents compression of the liquid, and FJ expansion of the vapour at the same constant temperature. The complete isothermal LDEFJ is a discontinuous curve with sharp breaks at the beginning and end of condensation.

Andrews showed that it was possible to effect the transformation

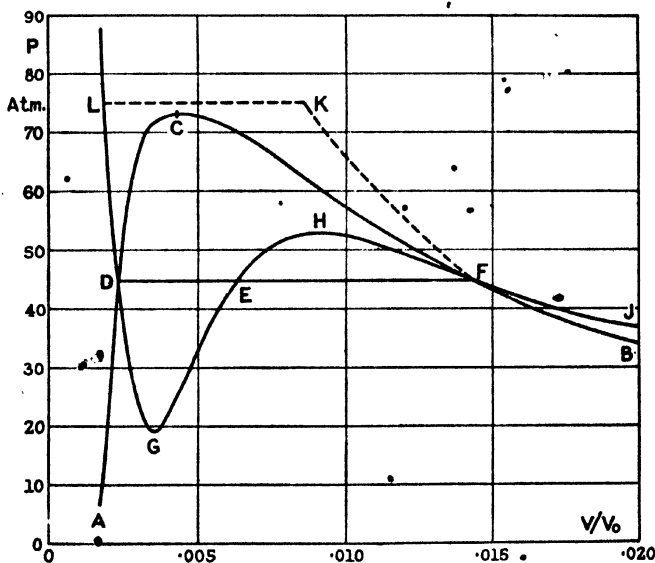


Fig. 17. James Thomson Isothermal for  $\text{CO}_2$  at  $10^{\circ}\text{C}$ .

from saturated vapour at F to saturated liquid at D, without any separation into two states, or breach of homogeneity, as follows. The substance is compressed and simultaneously heated along any line such as FK (which represents the adiabatic), to a temperature and pressure above the critical point. The state at K is evidently that of superheated vapour. The substance is then cooled, keeping the pressure constant, to its original temperature, when its state will be that represented by the point L. In passing from K to L, the substance remains homogeneous throughout. No separation of liquid and vapour occurs, but the substance at L is certainly in



the liquid state. This is shown by releasing the pressure to its original value. The liquid expands to D, at which point the vapour usually makes its appearance on further expansion. It is frequently possible, however, if the liquid is very carefully freed from dissolved air, to follow the expansion of the liquid several atmospheres below the saturation pressure, along the curve DG, which is an exact continuation of LD. But when the pressure is  $P$  atmospheres below saturation, a very small bubble, of radius only  $4Y/3P$  millionths of a cm. (if  $Y$  is the surface tension in  $\text{mgm./cm.}$ ) will suffice to start the vaporisation explosively, and restore the pressure to the saturation value. (*Ency. Brit.* 1911, vol. 27, p. 898.)

The dry saturated vapour can similarly be compressed, in the absence of liquid or hygroscopic surfaces, along the curve FH, which is an exact continuation of JF, to pressures considerably exceeding the saturation pressure. A limit of eight times the normal saturation pressure has been reached in the case of steam under suitable conditions at low temperatures. The vapour in this state is said to be supersaturated, a condition which appears to be very common in rapid expansion, such as occurs in a turbine nozzle. But since under this condition a dust particle of radius  $2Yv/RT\epsilon$  (where  $\epsilon$  is the pressure-ratio), is capable of acting as a condensation nucleus, this branch of the curve cannot be traced very far by static experiments. See X (23).

Since the transformation from vapour to liquid, or *vice versa*, can be effected by a continuous process without any breach of homogeneity, it is theoretically possible to include both states, liquid and vapour, in a single characteristic equation connecting the variables  $P$ ,  $V$ , and  $T$ , and representing an isothermal curve on the  $PV$  diagram for any given value of  $T$ . Considering the isothermal as an equation for finding  $V$  when  $P$  is given, experiment shows that for any isothermal above the critical temperature there can be only one real root representing the volume of the vapour at the given temperature and pressure. Below the critical temperature, James Thomson (*Proc. R. S.*, 1871) argued that the equation of the isothermal must have three real roots, such as  $D$ ,  $E$ ,  $F$  (for any given value of  $P$  within certain limits), two of which evidently correspond with possible volumes of the liquid and vapour, which can be observed experimentally along the branches LDG and HFJ respectively. These two branches should be parts of a single continuous curve such as LDGEHFJ on the indicator diagram, representing a continuous transformation from

liquid to vapour without breach of homogeneity, of which the middle part GEH, giving the third root  $E$ , is theoretically possible, but cannot be realised in practice because it represents a series of unstable states in which the volume increases with the pressure. It is possible, however, as J. Thomson suggested, that states corresponding to this part of the curve may exist in the surface film, which is in a different condition to the rest of the liquid.

**77. Van der Waals' Equation.** The simplest algebraic equation capable of representing the James Thomson isothermal is that proposed by Van der Waals in his celebrated essay on the "Continuity of the Liquid and Gaseous States" (Leyden, 1873) in the following form

$$(P + a'/V^2)(V - b) = RT. \dots\dots\dots(24)$$

The term  $a'/V^2$ , called the "internal" pressure, was identified with the capillary pressure of Laplace. It was attributed by Van der Waals to molecular attractions, and assumed to be proportional to the square of the density, but independent of the temperature. The constant  $a'$  being the same for liquid and vapour, the surface tension would vanish when the volumes and capillary pressures became equal at the critical point. We have already seen that a term of this type, as in Rankine's equation, represents the deviations of the vapour from the ideal state with a fair degree of approximation provided that the coefficient  $a'$  is a suitable function of the temperature, but according to P. G. Tait it cannot represent the properties of any known liquid.

The covolume  $b$  expresses the effect of the size of the molecules in reducing the free-space. Van der Waals showed that, according to the kinetic theory of gases,  $b$  should approximate to a constant limit when  $V$  is large, but should diminish with diminution of  $V$ . Boltzmann at a later date obtained a more exact expression for  $b$  as a function of  $V$ , but this is of no practical importance when the volume is large, and becomes inapplicable when the volume is small. For practical purposes  $b$  cannot represent anything except the minimum volume at high pressures, and cannot be regarded as a function of the volume without introducing hopeless complications in the theory of the critical state where it is of paramount importance.

Van der Waals treated both  $a$  and  $b$  as constants, and calculated their values from Regnault's experiments on the pressure-co-

efficient and the compressibility. The values found in this way for  $\text{CO}_2$ , taking the unit of pressure as the standard atmosphere of 760 mm., and the unit of volume as that of the gas at  $0^\circ \text{C}$ ., and 760 mm., were as follows:

$$a' = 0.00874, \quad b = 0.0028, \quad R = 1.00646/273. \dots (25)$$

With these values of the constants, the equation represents a fair qualitative approximation to the isothermal of James Thomson

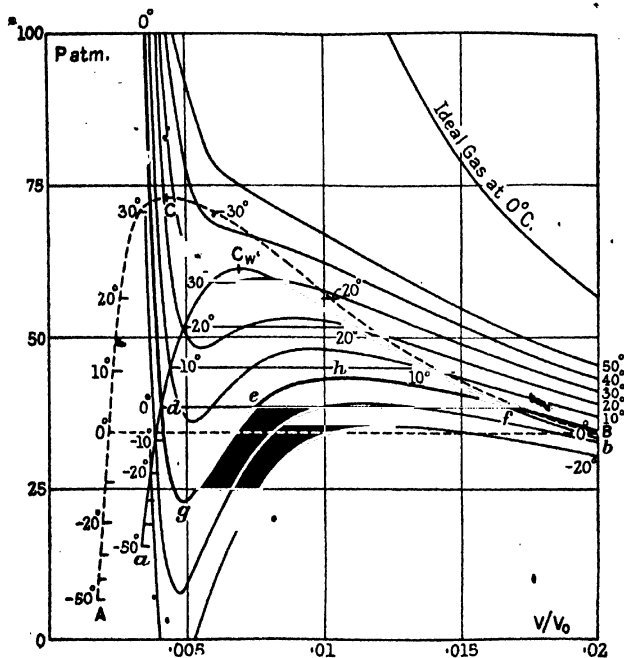


Fig. 18. Isotherms by Van der Waals' equation (24).

shown in Fig. 17, in which the scales of pressure and volume are the same as those employed by Andrews and Van der Waals, and subsequently adopted by Amagat. The saturation pressure 45 atmospheres at  $10^\circ \text{C}$ . cuts the Van der Waals isothermal in three points corresponding to DEF, Fig. 17, but the least root representing the volume of the liquid is nearly twice too large, and the volume of the vapour is a little too small.

The actual isotherms represented by Van der Waals' equation

for  $\text{CO}_2$  are drawn to scale at intervals of  $10^\circ \text{C.}$  from  $-30^\circ$  to  $+50^\circ \text{C.}$  in the annexed Fig. 18, in which the broken curve  $\text{ACB}$  represents the saturation volumes of liquid and vapour as observed experimentally, the full curve  $\text{AC}_w\text{b}$  those given by Van der Waals' equation. As the temperature is raised towards the critical point  $\text{C}_w$  the difference  $V - v$  diminishes, and the three roots approach equality. All three finally coalesce at the critical point, where the equation has three equal roots, and reduces to the form  $(V - V_c)^3 = 0$ ,  $V_c$  being the critical volume. Van der Waals deduced the values of the critical constants in the manner usually adopted in the theory of equations, namely, by writing equation (24) in the form of a cubic in  $V$  with unity for the coefficient of  $V^3$ , and equating the coefficients of the other powers of  $V$  to the corresponding coefficients in  $(V - V_c)^3$ . He thus obtained the well known relations for the critical volume, pressure, and temperature

$$V_c = 3b, \quad P_c = a'/27b^2, \quad T_c = 8a'/27bR. \dots\dots\dots (26)$$

Inserting the numerical values of the constants as given by (25), we find

$$V_c = 0.0069V_0, \quad P_c = 61.2 \text{ atmospheres,} \\ T_c = 305.3^\circ \text{ abs. or } t_c = 32.2^\circ \text{C.}$$

The approximate agreement of the calculated value of  $t_c$  with that observed by Andrews is still regarded as a remarkable verification of Van der Waals' theory, but little weight can be attached to this coincidence, because the value of  $b$  could not be determined with any approach to the required order of accuracy from Regnault's experiments. It was obvious that the critical pressure and volume did not show a satisfactory agreement with experiment, but, in order to make an adequate test of the theory, it was first necessary to find some method of calculating values of the saturation pressure at each temperature consistent with the form of the characteristic equation.

**78. Maxwell's Theorem.** The most important contribution to the theory of continuity of state on the thermodynamical side was that made by Clerk Maxwell (*Nature*, March 4, 1875, vol. 11, p. 358; *Collected Papers*, vol. 2, p. 434) shortly after the publication of Van der Waals' equation. There was no indication in the original theory of James Thomson, or of Van der Waals, as to how the horizontal line representing the saturation pressure should be drawn in relation to the continuous curve represented by the

equation at the corresponding temperature. Maxwell, by applying Carnot's principle, that no work could be obtained from heat without difference of temperature, showed that the saturation line on the indicator diagram DEF in Fig. 17, must cut off loops of equal area, DGE, EHF, from the continuous isothermal. The work represented by the area of each loop would then be the same, but the two would be of opposite sign, so that no work could be obtained from any heat-engine capable of performing the cycle, given by combining the curve DGEHF with the straight line FED. In other words, according to Maxwell's theorem, the work of vaporisation,  $p(V - v)$ , at saturation pressure  $p$  along the straight line FED must be equal to the work represented by the integral of  $PdV$  from  $v$  to  $V$  taken along the continuous isothermal DGEHF. The importance of this theorem is that it applies to any form of equation capable of expressing the continuity of state of liquid and vapour in a consistent manner.

Maxwell does not appear to have applied his theorem to the particular case of Van der Waals' equation, but the application is easily made by writing the equation in the form

$$aP/RT = 1/(V - b) - c/V^2, \dots\dots\dots(27)$$

where  $c$  is the coaggregation volume, equivalent to  $a'/RT$  in terms of Van der Waals' constant  $a'$ . The equation in this form is identical with that obtained by introducing the covolume  $b$  in Rankine's equation (20), except that  $c$  in (20) varies as  $T^{-2}$ , instead of being proportional to  $1/T$  as in (27).

Equating  $ap(V - v)$  to the integral of  $aPdV$  at constant  $T$  obtained from either equation (20) or (27), we find immediately

$$ap(V - v)/RT = \log_e(V - b) - \log_e(v - b) + c/V - c/v. \dots(28)$$

The form thus obtained for the equation of saturation pressure is extremely simple, but at the same time incredibly inconvenient for purposes of calculation. The values of  $V$  and  $v$  must satisfy the original equation (27) in addition to (28) so that there are three equations for determining  $p$ ,  $V$ , and  $v$  for any value of  $T$ , but the elimination of  $V$  and  $v$  cannot be effected so as to obtain an explicit relation between  $p$  and  $T$ .

The saturation pressures shown in Fig. 18 by the horizontal lines at each  $10^\circ$  from  $0^\circ$  to  $80^\circ$  C. were calculated from Maxwell's relation with Van der Waals' values of the constants  $a'$ ,  $b$ , and  $B$ . The curve  $aC_w$  extending from  $-50^\circ$  C. to the critical point, shows the values of the volume  $v$  of the liquid at saturation, with the

temperatures marked at intervals of  $10^\circ$  down to  $-50^\circ$  C. The curve  $C_{wb}$ , extending from the critical point to a little below  $0^\circ$  C., shows the corresponding values of the volume of the vapour  $V$  at saturation. The dotted curve  $ACB$ , shown in the same figure, represents the volumes of liquid and vapour actually observed in the case of  $CO_2$  at saturation, with the saturation temperatures similarly marked on the curve at the appropriate pressures. It will be seen that there is a wide discrepancy between the observed values of the saturation pressures and those calculated from Van der Waals' equation by the aid of Maxwell's theorem. The discrepancy in the value of  $V$  at  $0^\circ$  C. and saturation is only about 15 per cent., but the values of  $v$  deduced from Van der Waals' equation are all nearly double the values actually observed. The value of  $p$  is about right in the neighbourhood of  $12^\circ$  C., but the increase of  $p$  between  $0^\circ$  and  $80^\circ$  C. is nearly twice too small, and the value of  $p$  at  $-50^\circ$  C. is more than twice too large.

*Corollary.* It also follows from Carnot's principle as applied to the continuity of state that the latent heat  $L$  is given by the integral of  $aT (dP/dT)_v dv$  from  $v$  to  $V$  at constant  $T$ , which gives the simple expression  $L = RT \log_e (V - b)/(v - b)$ , for  $L$  according to Van der Waals' equation if  $a'$  is constant. The value of  $L$  at  $0^\circ$  C. comes out 25.6 cal. C., which is less than half the observed value, namely 54 cal. C., and the calculated values show a similar discrepancy from observation at other temperatures. But it is hardly to be expected that so simple an equation should be capable of satisfying all the required conditions.

It follows from the general expression for  $L$  when combined with Clapeyron's equation, that the useful coefficient  $dp/dt$  is equal to the mean value of  $(dP/dT)_v$  taken along the isothermal from  $v$  to  $V$  at equal intervals of  $v$ . The expression for  $L$  if  $c$  is any arbitrary function of the temperature, while  $b$  is constant, in an equation of the form (20) or (27), is easily seen to be

$$L = RT \log_e (V - b)/(v - b) + RT (T dc/dt + c) (1/V - 1/v), \dots (29)$$

which by substitution of  $ap (V - v)$  from (28) reduces to the form

$$L = ap (V - v) + T^2 (dc/dt) (R/V - R/v), \dots (30)$$

giving for  $dp/dt$  the simple and convenient expression

$$dp/dt = p/T - T (dc/dt) R/aVv, \dots (31)$$

in which it may be remarked that  $dc/dt$  is usually negative.

The equation of saturation pressure may also be obtained in a form identical with (28) by writing down the general expressions

for  $H$  and  $\Phi$ , and equating the values of  $G = T\Phi - H$  for liquid and vapour. The value of  $p$  at any temperature depends only on the values of the constants  $R$ ,  $b$ , and  $c$  at that temperature. If the critical temperature and pressure are known, the constants are readily determined from the critical relations

$$RT_c/ap_c = 8V_c/3 = 8b = 64c_c/27, \dots\dots\dots(82)$$

which apply to any equation of the type (20) or (27).

The absolute values of the constants for any particular substance can be eliminated by taking the ratios of each to their critical values, so that it is possible to construct a table of corresponding values of the ratios  $pT_c/p_cT$  and  $c_c/c$ , from which the value of  $p$  at any temperature is readily obtained in terms of  $c$ , or *vice versa*. Clausius (*Phil. Mag.*, vol. 13, p. 182, 1882) constructed a table of this kind, which gives also the corresponding values of  $V - b$  and  $v - b$  at saturation in terms of  $V_c - b$ . Similar tables can be constructed for other types of equation, but are very troublesome to calculate accurately, though useful in testing the applicability of any equation to a particular substance. Since it is always possible to choose the variation of  $c$  with temperature in such a way as to fit the observed variation of  $p$ , the applicability or otherwise of an equation cannot be determined by  $p$  alone, as is often assumed, and it is necessary to consider other properties in addition to  $p$ .

**79. Clausius' Equation for  $\text{CO}_2$ .** Of all the equations employed for  $\text{CO}_2$ , that of Clausius has been most often quoted, since it was realised that the equation of Van der Waals was very inaccurate. Clausius (*loc. cit.*) adopted Rankine's formula for the variation of  $c$ , but substituted  $V + b''$  for  $V$ , choosing the empirical constant  $b''$  to make the volume of the liquid agree with observation in the neighbourhood of  $20^\circ \text{C}$ .

$$aP/RT = 1/(V - b') - c/(V + b'')^2. \dots\dots\dots(83)$$

The effect of this is to reduce all the values of  $V$  and  $v$  by the constant quantity  $b''$ , and to replace  $V - b$  in the first term by  $V - b'$ , where  $b' = b - b''$ . The values of  $c$  and  $b$ , calculated from the critical relations (82), remain exactly the same as for (20).

If  $t_c = 81.5^\circ \text{C}$ , and  $p_c = 1071 \text{ lbs.}$ , as in Table IV, we have  $c_c = 0.05265$ ,  $c_0 = 0.0655$ ,  $b = 0.0156$ , F.P.C., as in (20), but  $b' = 0.0064$ , and  $b'' = 0.0092$ , to make  $v = 0.02078$  at  $20^\circ \text{C}$ .

For any given values of  $P$  and  $T$ , the value of  $V$  from (20) is

the same as that of  $V + b''$  from (33), and all the other properties calculated from (20) are identical with those calculated from (33) if Maxwell's theorem is assumed. The following table shows the values of the latent heat, saturation pressure and liquid volume, calculated with the aid of Clausius' table. The values apply equally to (20) or (33) except for the constant difference  $b''$  in  $v$ .

Table VII. Values of  $p$ ,  $L$ , and  $v$ , calculated from Clausius' equation.

t° C.	$p$ lbs./in. <sup>2</sup>		$L$ cala. G.		100 $v$ cu. ft./lb.		
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc. (20)	Calc. (33)
- 50°	97.2	64.5	80.0	109.6	1.386	1.944	1.024
- 20°	284.0	240.8	66.2	85.0	1.552	2.168	1.248
0°	505.1	468.2	54.1	65.9	1.731	2.433	1.513
+ 20°	829.0	812.1	36.5	39.6	2.075	2.993	2.073
+ 30°	1037	1034	(15.4)	14.3	—	3.891	2.971

Equation (20) gives 0.0468 for the critical volume, the same as Van der Waals' equation (27), but (33) gives  $0.0468 - b'' = 0.0376$ , which is in rather better agreement with Amagat's 0.0345 F.P.C. Unfortunately the values of the saturation pressure calculated by Maxwell's theorem (28), and those of the latent heat calculated by (29) or (30), do not agree sufficiently well with experiment to be of any practical use, at low temperatures. Clausius took 77 atmospheres at 31° C. for the critical pressure, in order to make  $p$  agree more nearly with observation at 0° C. But this value of  $P_c$  is undoubtedly too high, and does not materially affect the values of  $L$ , besides leaving  $p$  much too small at low temperatures. It would be possible, as already explained, to choose the variation of  $c$  to make the values of  $p$  agree as closely as desired with observation, but when this is done the equation no longer represents the variation of  $H$ , or the observed values of  $S$  and  $C$  satisfactorily, and the volumes of the liquid do not agree with observation any better than before.

The same difficulty is illustrated by Clausius' equation for Steam (*loc. cit.*), which is of the same type as (33), but with different values of the constants, which are as follows:

$$b' = 0.000754, \quad b'' = 0.001815,$$

$$c = 45.17T^{-1.24} - 0.00787, \text{ in cu. m./kg.}$$

The variation of  $c$  was chosen to fit with Regnault's values of the saturation pressure from 0° to 220° C. The values of  $c$  calculated in this way do not represent the cooling-effect satisfactorily, and the



extrapolated values given by the equation at the critical point, namely,

$$t_c = 382^\circ \text{C.}, \quad p_c = 134 \text{ atmospheres}, \quad V_c = 0.589 \text{ c.c./gm.}$$

differ widely from the results of experiment. The constant  $b''$  was chosen by Clausius to fit the volume of the liquid at  $20^\circ \text{C.}$ , but the volumes of the liquid at other temperatures do not agree at all with observation.

Table VIII. Volumes of Water from Clausius' equation for steam.

Temp. Cent.	0°	100°	200°	300°	332°
Vol. Obs. c.c./gm.	1.000	1.0433	1.159	1.429	1.620
„ Calculated	0.971	1.160	1.526	2.686	5.89

It is unjustifiable to apply Maxwell's theorem for calculating the saturation pressures, or deducing the values of the constants in any equation, unless it is capable of representing the properties of the liquid with the same degree of proportionate accuracy as those of the vapour. An equation of the Van der Waals type, with  $c$  a suitable function of  $T$ , is fairly accurate for representing the properties of the vapour through a wide range, but it is most inconvenient and unsuitable for the liquid, and it may be doubted whether it is possible to represent the properties of both liquid and vapour by a single formula without impracticable complications which would render such an equation useless.

### 80. Variation of $H$ , $S$ , and $C$ near the Critical Point.

The critical point is most conveniently defined by the general conditions

$$(dP/dV)_c = 0, \quad \text{and} \quad (d^2P/dV^2)_c = 0, \quad \dots\dots\dots (84)$$

which imply that it is a point of inflexion on the indicator diagram with a horizontal tangent cutting the critical isothermal in three consecutive points. The expression for  $(dP/dV)_c$  on the critical isothermal contains  $(V - V_c)^3$  as a factor, and becomes zero of the second order at the critical point, where  $V = V_c$ , vanishing without change of sign.

It follows from the general expressions (14) and (15) for  $SC$  and  $S$ , that both will become infinite of the second order at the critical point, but since the only term in  $S$  which becomes infinite is that containing  $SC$  as a factor, we observe that  $C$  remains finite, being equal to the reciprocal of  $(dP/dT)_c$  at the critical point, and

that  $C(dP/dT)_c$  differs from unity by a small quantity of the second order only, if  $(dH/dT)_c$  remains finite.

We have already seen as a corollary to Maxwell's theorem that  $dp/dt$  is a mean between the values of  $(dP/dT)_g$  for the liquid and vapour which become equal at the critical point.

At the critical point

$$1/C = (dP/dT)_c = dp/dt. \dots\dots\dots(85)$$

This is a useful relation, which has generally been overlooked, for testing the applicability of an equation at the critical point, because an expression for  $(dP/dT)_c$  is easily found from the equation, and compared with the observed value of  $dp/dt$ , which is generally known with a fair degree of accuracy. Thus in the case of (20) or (83), we have  $dc/dt = -2c/T$ , so that  $dp/dt$  at the critical point from (81) and (82) comes out exactly  $7p/T$ . But the empirical equation (1), which cannot be far out, makes it only  $6.5p/T$ , so that we should expect to find some difficulty, as is shown to be the case by Table VII, in reconciling (20) or (83) with the saturation pressures, unless the index of  $c$  were reduced.

One of the commonest objections to an equation of the Van der Waals type is that it makes the ratio,  $RT_c/ap_cV_c$ , of the ideal volume to the critical volume, equal to  $8/3$ , as shown in (82), whereas experiment gives higher values, averaging 3.7 for most substances. This is not a fatal objection because Maxwell's theorem says nothing about the zero from which  $V$  is reckoned, but gives only  $V_c + b''$ , so that  $V_c$  can usually be adjusted to suit the observations by the method of Clausius.

Dieterici (*Ann. Phys.*, vol. 5, p. 51, 1901) devised a very ingenious equation, which is often quoted, to meet this objection, namely,

$$aP(V - b) = RTe^{-c/V}. \dots\dots\dots(86)$$

Applying conditions (84) we obtain for the critical relations

$$V_c = 2b = c_c/2, \quad RT_c/ap_c = e^{2b} = 7.39b = 3.695V_c, \dots(87)$$

giving the required value 3.7 for the critical ratio without any adjustment. This equation gives a simple expression for  $SC$ , and very fair agreement with observed values of  $C$  from  $-30^\circ$  to  $+80^\circ$  C., if  $c$  is assumed to vary as  $1/T^{3/2}$ , as proposed by Dieterici. Unfortunately the expressions for  $L$ ,  $p$ , etc. cannot be integrated in finite terms. This would not be a serious matter if the equation were otherwise satisfactory. We find, however, by applying con-

dition (33), that the value of  $dp/dt$  at the critical point is only  $\frac{1}{2}p/T$ , showing that it would be impossible to reconcile the saturation pressures with experiment, unless the index of  $c$  were raised to 2.75, in which case it would not represent the other properties at all satisfactorily.

Another suggestion with a similar object is to reduce the index of  $V$  in the term  $c/V^2$  in Van der Waals' equation from 2 to  $5/3$ . This gives a value 3.75 for the critical ratio. But it also gives  $dp/dt = 9p/T$  at the critical point, if the index of  $c$  is 2, and would require the index of  $c$  to be reduced to  $11/8$  to agree with the saturation pressures. This would not affect the value of  $V_c$ , or of  $c_c$ , which is  $16V_c^3/15$ , but the equation would be unsatisfactory for the representation of the cooling-effect. Thus, it would make  $C$  at  $0^\circ\text{C}$ . about 30 per cent. too large at saturation, diminishing to negative infinity at zero pressure, and the two fractional indices would be very inconvenient as compared with the simple squares in (20) or (33). Most of the other numerous modifications which have been proposed appear liable to similar objections. Attention has usually been restricted to the representation of some particular property, such as the saturation-pressure, without observing that modifications introduced with this object played havoc with the other properties of the substance. Clausius devoted his attention almost exclusively to the saturation-pressures, which he did not succeed in representing very accurately, but he appears to have been quite unaware that the chief merit of the equation lay in representing the total heat.

It has often been disputed, whether the volumes of the liquid and vapour actually become equal at the critical point when the surface tension vanishes. There is strong evidence that the capillary elevation  $y$  of the liquid in a tube of radius  $r$  diminishes near the critical point at a finite rate, and vanishes precisely at the critical temperature. But the surface tension,  $Y = g\gamma r (V - v)/2Vv$ , also contains the factor  $V - v$ , so that  $dY/dT$ , and the surface energy  $Y - TdY/dT$ , should vanish simultaneously with  $Y$  when the volumes become equal. In the case of mixtures there are many possibilities, but in the case of a pure substance there is no satisfactory reason to abandon the simple relations  $V = v$ , and  $L = 0$ , consistent with an equation of the Van der Waals type, or to assume that any molar distinction between liquid and vapour can persist beyond the critical point, though both types of molecules may remain present in the mixture.

Assuming that the latent heat vanishes, and that the saturation values of the total heats of liquid and vapour become equal at the critical point, the rates of variation of  $H$  and  $h^s$  must become infinite, but with opposite signs. This is consistently explained by the usual equation III (7) for the variation of the total heat at saturation, when combined with (15), which gives

$$(dH/dT)_s = (dH/dT)_v + SC [(dP/dT)_v - (dp/dt)_s] \dots (38)$$

The coefficient  $(dH/dT)_v$  remains finite, and becomes the same for liquid and vapour at the critical point, but  $SC$  becomes infinite of the second order. The value of  $dp/dt$  is intermediate between those of  $(dP/dT)_v$  for the liquid and vapour, so that the difference in square brackets is positive for the liquid but negative for the vapour. Since this difference is a small quantity of the first order near the critical point, the product of the difference by  $SC$  becomes infinite of the first order at the critical point, but changes sign from positive to negative in passing from liquid to vapour. This gives a perfectly consistent representation of the phenomena in the neighbourhood of the critical point, agreeing with the values of the coefficients given by an equation of the Van der Waals type in conjunction with Maxwell's theorem, but material inconsistencies may result if experimental values of  $dp/dt$  are employed which do not happen to agree with those of  $H$  and  $SC$  and  $(dP/dT)_v$  required by the characteristic equation or the expression for  $H$ .

**81. Equation of Saturation Volume.** An equation of the Van der Waals or Clausius type represents the properties of the liquid so badly that it would seem almost hopeless to apply Maxwell's theorem, with any empirical adjustment of  $c$  to make the saturation pressures correct, because it would certainly follow that the equation, being inconsistent for the liquid, would be also erroneous in several other respects. Van der Waals' theory of the covolume and the capillary pressure is very unsatisfactory as applied to the liquid; but a term  $c/V^2$  of the Rankine type may be interpreted as representing the effects of coaggregation in the vapour, according to the law of equilibrium between molecules of different types, at moderate pressures, and the covolume  $b$  introduces the necessary limit at high pressures, so that the equation remains a very suitable type of empirical formula for the vapour, although the theory cannot be regarded as exact. Any attempt to modify this type to suit the liquid would probably result in such

intolerable complexity, that it is preferable to assume *different* equations for the liquid and vapour.

The simplest method of obtaining a consistent equation of saturation volume is that employed by the author in the case of steam, namely to assume an equation of the type (4) for the total heat of the liquid, which has already been shown to give satisfactory agreement with experiment. This equation, when combined with (20) for the vapour, will necessarily give a fair approximation to the saturation pressures, so far as (20) correctly represents the total heat of the vapour. As in the case of steam, we have merely to integrate equation (4) with the expression for  $H$  from (20), which is easy, because  $H - aVTdp/dt$  when divided by  $T^2$  is necessarily the exact differential of  $G/T$ , namely

$$(1/T) dG/dT = G/T^2.$$

The equation thus obtained gives values of the latent heat and saturation pressure from  $-50^\circ$  to  $+28^\circ\text{C.}$ , which are much better than those obtained from Maxwell's theorem, as given in Table VII. But it fails near the critical point to give any solution, for the reason already explained, namely that the saturation pressures cannot be reconciled with the value  $dp/dt = 7p/T$  at the critical point required by equation (20), or by (33), which cannot be corrected by changing the index of  $c$  without introducing other discrepancies.

There is an infinite variety of ways in which the equation may be modified to suit the critical conditions, especially if transcendental functions are introduced, but the experimental evidence is too vague to determine the form of the equation with any certainty. For this reason it seems preferable to limit the field to algebraic equations of the cubic type, which are well understood and fairly easy to manipulate. The following equation does not appear to have been investigated previously

$$aP/RT = 1/V - c'/V^2 + c''/V^3, \dots\dots\dots(39)$$

in which  $c'$  and  $c''$  are any arbitrary functions of the temperature. This equation is based on the coaggregation theory, but, since no such theory can claim to be exact for very high densities, it is better to regard the equation simply as a convenient type of empirical formula for the vapour. The application of the critical conditions (84) gives immediately

$$aP_c/RT_c = 3V_c = 3c'_c = 9c''_c, \dots\dots\dots(40)$$

which are simpler than those given by the Van der Waals type,

and give a somewhat better value of the critical ratio. The co-aggregation theory requires that  $c'$  shall be of the form  $c - b$ , where  $c$  is the usual coaggregation volume and  $b$  the covolume. If we restrict ourselves to squares and square-roots, which are easy to work on a slide-rule,  $c$  must vary inversely as the square of  $T$ , as in Rankine's equation, and  $b$  directly as the square root, and the value of  $c''$  must be  $5b/3$ , in order to satisfy (40) and to make the value of  $dp/dt$  exactly  $6.5p/T$  at the critical point. We thus obtain

$$V_c = c - b = 5b = 0.0416 \text{ F.P.C.} \dots\dots\dots(41)$$

When the constants are determined in this way at the critical point, the values obtained for the specific heat and the cooling-effect are very nearly the same as those given by equation (20), which have already been verified. But (39) has the advantage of giving very accurate values of the saturation pressure all the way from  $-30^\circ$ , and of giving an exact solution right up to the critical point. The pressures are also within 2 per cent. of Amagat's along the  $40^\circ$  isothermal down to a point well below the critical volume. The saturation volumes agree with Amagat's at  $0^\circ$  and  $10^\circ \text{C.}$ , and are probably within the limit of experimental error at  $80^\circ$ . The equation also gives a much closer approximation than (20) to the liquid volumes, though not good enough to permit the application of Maxwell's theorem.

Combining equation (39) with (4), the equation to be integrated for the saturation volumes reduces to the simple form

$$L'_c + 0.217t' = aVTdp/dt + DH, \dots\dots\dots(42)$$

where  $DH$  is the defect of the total heat according to (39) from the ideal value  $S_m t + B$  at zero pressure.  $L'_c$ , the ideal value of the latent heat, is the critical value of  $aVTdp/dt + DH$ , which is exactly  $5RT_c$ , according to (39). The constant 0.217 is the difference of the specific heats of the liquid and vapour, as in the corresponding equation for steam, and  $t'$  is the temperature  $t_c - t$ , reckoned downwards from the critical point, which is one of the limits of integration, the other being the saturation volume  $V$  at  $t'$ .

The integral of this equation corresponds term by term with that similarly obtained for steam in Chapter VII, equation (18), except that the limits are different, and that an equation of the form (39) necessarily gives the relation between temperature and saturation volume instead of saturation pressure. When the volume

is found, the pressure is given by (39). The equation of saturation volume takes the form

$$4mt'/T + 5.81 [mt'/T - \log T_c/T] \\ = \log V/V_c + 2mc'/V - 5mbc'/2V^2 - 3m/2, \dots (43)$$

in which the logarithms are to the base 10, and  $m$  is the modulus of common logarithms. The coefficient 4 in the first term is  $L_c'/RT_c - 1$ , and the coefficient 5.81 in the second term is  $1 + 0.217/R$ . The symbol  $t'$  denotes  $t_c - t$ , and the symbol  $c'$  denotes  $c - b$  as in (40). The constant  $3m/2$  is the difference of the two preceding terms at the critical point. The temperature function in square brackets in the second term on the left is a small quantity of the second order near the critical point, but becomes important at low temperatures. It is easy to find the value of  $V$  from this equation for any given  $t'$ , by taking a trial value of  $V$  from Table IV in calculating the volume function on the right hand side of the equation. After two trials, the solution is obtained by interpolation. Near the critical point, it is necessary to use seven-figure logarithms, and to take values of  $c$  and  $b$  exactly consistent with those assumed at the critical point, because the volume function reduces to a small difference between relatively large quantities, but an error in  $V$  makes very little difference in the pressure at this point.

The following table shows a comparison of the results calculated from (43) with those given by observation so far as they can be verified.

Table IX. Values calculated from (39) and (43) in F.P.C. units.

$t$	$p$ (43)	$p$ (K. & R.)	100 $v$	100 $V$	$h$	$H$	$L$ (43)	$L$ (3)	$S_s$	$s_s$
- 60°	63.2	63.2	1.345	137.7	29.92	55.64	85.50	—	—	—
- 50°	97.2	97.0	1.386	91.25	25.57	56.51	82.08	80.00	0.215	0.46
- 40°	143.6	144.0	1.433	62.44	20.98	57.17	78.15	75.77	0.231	0.48
- 30°	205.0	205.2	1.488	43.83	16.16	57.54	73.70	71.20	0.252	0.50
- 20°	284.0	284	1.552	31.34	11.15	57.54	68.69	66.21	0.282	0.53
- 10°	383.1	383	1.631	22.72	- 5.77	57.08	62.85	60.55	0.326	0.57
0°	505.1	505	1.731	16.57	0	56.02	58.02	54.06	0.398	0.63
+ 10°	652.9	653	1.866	12.02	+ 6.33	54.08	47.75	46.21	0.538	0.735
15°	737.3	735	1.957	10.17	9.82	52.63	42.81	41.44	0.670	—
20°	820.0	828	2.075	8.490	13.69	50.63	36.94	36.55	0.923	0.995
25°	928.5	930	2.272	6.916	18.25	47.70	29.45	29.18	1.581	—
28°	992.2	994	2.482	5.943	21.75	44.98	23.23	22.59	2.993	—
30°	1036.5	1038	2.756	5.210	25.07	42.15	17.08	15.92	5.981	—
31°	1058.4	1062	3.073	4.719	28.14	39.80	11.66	10.11	20.76	—
31.5°	1070.0	1071	4.160	4.160	36.32	36.32	0	0	Inf.	—

The values of the saturation pressure  $p$  given by (48) are compared with the observations of Kuenen and Robson below  $0^\circ \text{C.}$ , interpolated where possible from the actual observations, since the values in their table are less accurately stated. The empirical formula (1) agrees better than (43) with the observations of Zeleny and Smith at low temperatures, but a formula of the type (1) necessarily gives too high values in this region, and the observations of Kuenen and Robson appear the most reliable from internal evidence. Amagat's values are taken above  $0^\circ \text{C.}$ , but are uncertain by 2 or 3 in the last figure.

The values of  $v$  are taken as in Table IV, up to  $+20^\circ \text{C.}$  from Behn's observations. Beyond this point they are calculated to suit the critical volume  $0.0416 \text{ F.P.C.}$  They differ from Amagat's by less than 3 per cent. at  $31^\circ \text{C.}$ , where the observations would be extremely uncertain, and the rectilinear diameter might well present singularities.

The discrepancy between Tables IV and IX in regard to the values of  $V_c$  and  $H_c$  looks alarming at first sight, but is of no practical importance, because the values of  $V$  or  $H$  near the critical point cannot be accurately specified in terms of  $P$  and  $T$ . The relation between  $H$  and  $V$  near the critical point remains practically the same in both tables. Thus the formulae of Table IV would give  $H = 36.3$  at  $V = 0.0416$  as in Table IX, and the formulae of Table IX give  $H = 31.4$  at  $V = 0.0344$ , as in Table IV. The uncertainty of Table IV, from a theoretical standpoint, lies in the assumption of a rectilinear diameter of  $1/V$  and  $1/v$ . If we had assumed a rectilinear diameter of  $H$  and  $h$ , which is intrinsically more probable, but unorthodox, we should have found  $H_c = 34.4$  instead of  $31.4$ , giving  $V_c = 0.0386$  instead of  $0.0344$ .

The values of  $h$  in Table IX differ slightly from those in Table IV. The reason of this is that the limiting value of the specific heat of the liquid,  $0.42$ , was assumed to be constant in calculating Table IV, in the absence of evidence to the contrary, whereas in Table IX the difference of the specific heats of liquid and vapour at zero pressure was assumed to be constant, and to be equal to the value,  $0.420 - 0.203 = 0.217$ , at the critical point. This is intrinsically more probable, and has the effect of simplifying the equations (42) and (43). It also gives better agreement with the observed values of  $p$  and  $h$ , and tends to reduce the discrepancy in the values of  $L$ .

By far the most serious difference is that between the observed



and calculated values of  $L$ , which has already been illustrated in Fig. 16. The values given in Table IX under the heading  $L$  (48) are calculated from consistent values of  $V$  and  $dp/dt$ , deduced from the same equation, and have greater weight than values of  $L$  previously calculated by Mollier, Cailletet, and others, from independent and possibly inconsistent observations, such as those of Regnault for  $p$ , and Cailletet for  $V$ . The values  $L$  (48) are represented by the broken curve in Fig. 16, which gives an exact continuation of the curve representing Amagat's table down to  $1^{\circ}$  C. The values  $L$  (8) are taken from equation (8) representing Jenkin and Pye's observations, with the exception of the observation at  $20^{\circ}$  C. which falls on Amagat's curve. Above this point the values under  $L$  (48) depend on an empirical extrapolation of the values of  $v$ , which are more uncertain, but do not differ greatly from Amagat's.

The required expression for  $H$  is deduced from equation (39) in the same way as in the case of Rankine's equation (9). Differentiating (39), with regard to  $T$  at constant  $V$ , we find

$$a(dP/dT)_v = R/V + (c + 3b/2)R/V^2 - 5b(c + 4b)R/6V^3. \dots(44)$$

The expression for  $E$  is deduced by integrating  $aT(dP/dT)_v - aP$  at constant  $T$  with respect to  $V$ , from  $V = \text{infinity}$  to  $V$ , and  $aPV$  is added to find  $H$ .

$$H = S_m t + B - (3c - b/2)RT/V + 5b(7c - 2b)RT/12V^2. \dots(45)$$

$SC$  and  $S$  are obtained by differentiation as in (14) and (15),

$$SC = a[3c - b/2 - 5b(7c - 2b)/6V]/[1 - 2(c - b)/V + 5b(c - b)/V^2], \dots\dots(46)$$

$$S = S_0 + 3(c + b/4)R/V - 5b(7c + 8b)R/24V^2 + SC(dP/dT)_v. (47)$$

To find  $L$  and  $h$  at saturation for any value of  $T$ ,  $V$  is first calculated from (48).  $H$  and  $DH$  are obtained from (45).  $DH$  in (42) is  $S_m t + B - H$ , which gives  $aVTdp/dt$ , taking  $L' = 5RT = 68.68$ , whence  $avTdp/dt$  for the liquid (since  $v$  is known) and the difference gives  $L$ .  $H - L = h$ , which may also be obtained directly from the equation

$$h = (S_m + 0.217)t - 6.53 + avTdp/dt. \dots\dots\dots(48)$$

The constant being chosen to make  $h = 0$  at  $0^{\circ}$  C., gives  $B = 68.97$  in (45).

The expressions for  $S$  and  $SC$  are useful for calculating consistent values of either near the saturation line, or in other cases

where they cannot be measured experimentally. The values of  $S_s$  given in Table IX were calculated in this way from (47) by using the saturation values of  $V$ . They are chiefly of academic interest, and illustrate the rapid variation of  $S$  near the critical point.

The values of  $s$ , given in the table are those of the specific heat of the liquid at constant pressure at the saturation point. They are obtained from  $dh/dt$  by the usual relation, III (7),

$$s_s = (dh/dt)/(1 - Cdp/dt), \dots\dots\dots(49)$$

in which  $C$  denotes the cooling-effect for the liquid at saturation. The results agree closely at low temperatures with the observations of Jenkin and Pye on the specific heat of the liquid at constant pressures of 700 and 900 lbs., because the values of  $C$  are small and fairly certain. Above  $0^\circ \text{C}$ . the values of  $C$  become more uncertain, and the values of  $s$  show an increasing divergence from the observations at lower temperatures, because both  $s$  and  $C$  increase rapidly in the neighbourhood of saturation. They cannot be calculated above  $20^\circ \text{C}$ . without assuming some arbitrary type of characteristic equation for the liquid.

**82.  $H \log P$  Diagram for  $\text{CO}_2$ .** The annexed diagram is given as a graphic illustration of the properties of a substance in the critical state. On account of the experimental discrepancies previously enumerated, which amount to nearly 4 per cent. in the value of the latent heat at  $0^\circ \text{C}$ ., the diagram cannot claim a very high order of quantitative accuracy, but there is no other substance for which more complete and accurate data are available in this region, and there is little doubt that the diagram for  $\text{CO}_2$  affords a very fair qualitative representation of the phenomena.

Mollier (*Zeit. Ver. Deut. Ing.*, vol. 48, p. 272, (1904)) gave an  $H\Phi$  diagram for  $\text{CO}_2$  together with his well known diagram for steam. In constructing a diagram of the  $H\Phi$  type near the critical point, it is necessary to use skew coordinates in place of rectangular, because the pressure and temperature lines would otherwise be excessively crowded. Both pressure and temperature lines are of a peculiar shape and difficult to locate accurately, which makes it difficult to construct the  $H\Phi$  diagram from experimental data. Mollier also gave an  $HP$  diagram, which is much easier to construct, and possesses some useful properties, but affords an inconvenient scale, when extended to low pressures. The scale of temperature in the wet

region is five times as open near the critical point as at  $-50^{\circ}\text{C.}$ , and the volume lines are excessively crowded at low pressures. The adiabatics are also of an inconvenient shape, being sharply curved near the lower extremity. These difficulties are avoided by taking the *logarithm* of the pressure as one of the coordinates, which gives uniform proportionate accuracy in reading the pressures. The adiabatics become nearly straight, and it is possible to insert a complete system of constant volume lines without confusion.

There is little advantage in having the adiabatics exactly straight, as in the  $T\Phi$  and  $H\Phi$  diagrams, because adiabatic expansion or compression cannot be accurately realised in practice, and because the value of  $\Phi$  is seldom required and can never be observed experimentally. The quantity most often required is  $H$ , and that most easily observed is  $P$ . The processes most accurately realisable in practice are those of expansion through a throttle at constant  $H$ , and heating or cooling at constant  $P$ . It is a great convenience to have the lines of constant pressure straight, although it entails a logarithmic scale, but this cannot well be avoided in any case.

Mollier made use of Regnault's data for the saturation-pressures below  $0^{\circ}\text{C.}$ , and deduced an expression for the entropy from an equation of the Clausius type, but assumed  $c$  in equation (38) to be of the form,  $Ke^{(t_c - t)/T_c}/RT$ . He also assumed the specific heat at constant volume to be constant and equal to 0.182, which would be inconsistent with (33) and with Joly's experiments. Some of his lines of constant pressure are thermodynamically impossible, but the experimental data available in 1904 were very incomplete. Most of the deficient experimental data were supplied by Jenkin and Pyc (*loc. cit.*), who gave a more accurate  $H\Phi$  diagram, constructed on the same lines as that of Mollier, but directly from the experimental data without assuming any particular type of equation. There is much to be said for this method, on account of the uncertainty of the theory, if the object is merely to construct a diagram for practical use. But it is convenient to have a set of equations to represent the experimental data, if the object is to elucidate the theory, or to calculate properties which cannot be read with sufficient accuracy from a diagram.

The diagram here given was constructed at the same time as the steam diagram (1915) with a view of testing, in the critical region, the equation employed for the total heat of the liquid, and

the method of calculating the saturation pressure by combining the equation for  $h$  with a suitable type of characteristic equation, for the vapour. Both these methods were found to give more satisfactory results than any based on Maxwell's theorem, and there was no great difficulty in making the equation represent the variation of the total heat of the vapour satisfactorily. But it was found to be impossible to reconcile the values of the latent heat observed by Jenkin and Pye with values calculated from Amagat's observations, or from any form of characteristic equation consistent with the saturation-pressures and with the variation of  $H$  and  $h$ . This may possibly be explained by the restriction of the investigation to equations of the simple cubic type, but it is at least equally possible that there may be some constant error in the observations of  $L$ , if the great difficulties of the experimental measurements are considered.

In constructing the diagram, Fig. 19, Table IV was taken as the basis for the saturated state, which made it very easy to plot all the lines in this region, but implied the adoption of the experimental values of  $L$  represented by formula (3), in place of those deduced from Amagat's table or from the characteristic equation. The starting points of the lines of constant temperature and volume thus fixed on the saturation curve were necessarily inconsistent with those of Amagat above  $0^{\circ}\text{C}$ . The position of the isothermal at  $100^{\circ}\text{C}$ . was fixed with a fair degree of certainty by the characteristic equation, but some adjustment was required in spacing the intervening isothermals. This was found to be unsatisfactory, and it would be better, in drawing the diagram on a large scale for practical measurements, to draw all the curves for the vapour down to  $V = 0.04 \text{ F.P.C.}$ , including the saturation line, so as to be consistent with Table IX instead of Table IV. This is easily done with the aid of equations (39) for  $P$  and (45) for  $H$ , which though inconvenient for calculating  $V$  and  $T$  from  $H$  and  $P$ , are of a suitable type for locating the lines of constant temperature and volume on the  $HP$  diagram by calculating values of  $P$  and  $H$  for given values of  $V$  and  $T$ .

In the liquid region below  $20^{\circ}\text{C}$ . the lines of  $V$  and  $T$  are fairly simple and are readily drawn to fit the saturation line with the aid of Amagat's tables and of Jenkin and Pye's values of the specific heat and the cooling-effect. Near the critical point there is necessarily some uncertainty owing to the absence of observations on  $S$  and  $C$ , but some assistance is obtained from the consideration

that the relation between  $V$  and  $H$  remains finite and continuous being represented by the relation, App. I, (55),

$$^*(dV/dH)_p = C/aT + V/ST = (1/aT) (dt/dP)_p, \dots (50)$$

the value of which at the critical point is 0.00140 F.P.C.

The adiabatics, of which a few are shown dotted, present no

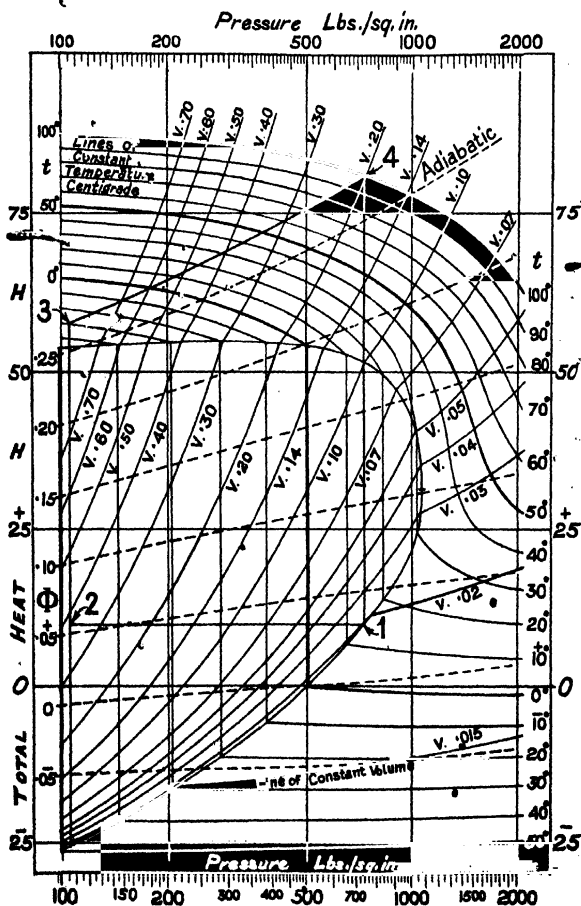


Fig. 19.  $H \log P$  Diagram for  $\text{CO}_2$ .

difficulty, since they cross the saturation line without change of direction, and the vertical scale of entropy is  $T$  cal./deg. in any part of the diagram.

The position of the critical point shown on the diagram is that deduced from the rectilinear diameter of  $1/V$  and  $1/v$ . It should probably be higher, as already explained, but this would not affect the position of the  $V$  lines appreciably, and would fit better with the raising of the saturation line for the vapour as required by Amagat's table and by equation (39).

**83. Refrigeration Cycle.** The method of Jenkin and Pye for measuring the latent heat affords a good example of the usual refrigeration cycle. The gas is compressed by a pump and liquefied continuously in a condenser. The liquid flows through weighing flasks (required in these special experiments for measuring the flow) past a thermocouple, where its temperature  $t_1$  is measured, to a throttle. In passing through the throttle from  $p_1$  to  $p_2$ , the total heat remains constant and equal to its value  $h_1$  on the saturation line at  $t_1$ , but some of the liquid evaporates and its temperature falls to that of saturation,  $t_2$  at  $p_2$ . It then passes through a calorimeter in which it is completely evaporated at constant pressure  $p_2$ , and is superheated to a temperature  $t_3$  (which is measured), to make sure of complete evaporation. The heat absorbed in this process is measured by observing the electric energy required to keep the temperature of the calorimeter constant, and is equal to the change of total heat from  $h_1$  as liquid before passing the throttle to  $H_3$  as vapour on leaving the calorimeter, applying corrections for any external loss or gain of heat in the process. The latent heat at  $t_2$  is deduced (1) by adding the difference  $h_1 - h_2$  between the values of the total heat of the liquid on the saturation line at  $t_1$  and  $t_2$ , and (2) by subtracting the difference  $H_3 - H_2$  required to superheat the vapour from  $t_2$  to  $t_3$ . After leaving the calorimeter, the vapour is returned to the pump, and compressed to the saturation pressure  $p_1$  in the condenser.

Jenkin and Pye illustrate the process in their paper by areas measured on the  $T\Phi$  diagram, but it is much easier to follow on the  $H \log P$  diagram. Taking one of their experiments as an example, the initial state as liquid before passing the throttle is represented by the point (1) on the saturation line at  $+14.7^\circ \text{C.}$ , where the total heat is  $h_1 = 9.77$  according to equation (4). It is throttled along the horizontal line at  $h = 9.77$  to the point (2), where the pressure is given as 105 lbs., and the temperature  $t_2 = -48.8^\circ \text{C.}$

By employing adiabatic expansion in place of throttling, work equal to the adiabatic heat-drop (5.7 as measured on the diagram) might be gained, with an equal increase in the refrigerating effect, but the theoretical gain would probably be counterbalanced in practice by mechanical losses, and the adiabatic process would in any case be inapplicable for accurate measurement.

The flow through the calorimeter during the experiment was 6 lbs., in 51.5 mins. The electric heat supply was 42.9 cal. per lb. The heat gained by the calorimeter externally was estimated as 5.8 cal. per lb., giving 48.2 cal. per lb. as the refrigerating effect  $H_3 - h_1$ , due to the evaporation, and to the superheating from  $-48.8^\circ$  to  $-30.6^\circ$  C., including an almost negligible correction for change of temperature of the calorimeter between the beginning and end of the experiment.

The quantity  $h_1 - h_2$  to be added, and the quantity  $H_3 - H_2$  to be subtracted from the observed refrigerating effect in order to deduce the latent heat,  $L = H_2 - h_2$ , were determined by special experiments. The change of  $h$  for the liquid, at constant pressures of 700 and 900 lbs., was observed over various ranges of temperature from  $-40^\circ$  to  $+19^\circ$  C. Combining these results with observations of the cooling-effect, the variation of  $h$  along the saturation line could be deduced. The correction  $h_1 - h_2$  is given as 35.25 by Jenkin and Pye for this particular experiment, agreeing as closely as possible with the value read on the  $H \log P$  diagram, from point (2) down to the liquid limit curve.

The correction  $H_3 - H_2$  for the superheating of the vapour was estimated by measuring the specific heat of the vapour near the saturation line, and is given as  $-3.72$  cal., which also agrees as nearly as possible with the distance of point (3) above the saturation line on the  $H \log P$  diagram. The value of  $L$  comes out 79.75, as shown on the curve in Fig. 16.

The difficulties of manipulation increase considerably at temperatures above  $10^\circ$  C., owing to the rapid variation of the quantities concerned, and the corrections become less certain, especially that for the superheat. Thus at  $20^\circ$  C. the specific heat at saturation according to Table IX is 0.92, but varies so rapidly that the change of  $H$  would be difficult to determine satisfactorily without the aid of an expression for  $H$  such as (45).

The standard refrigeration cycle is supposed to be completed by adiabatic compression to the condenser pressure  $p_1$  as shown by the line (8, 4) on the diagram. The work required is represented

by the difference  $H_4 - H_3$ , which is found to be 23.5 cal., as measured on the diagram for this example. The ratio  $(H_3 - h_1)/(H_4 - H_3) = 2.05$  called the "coefficient of performance," depends chiefly on the temperature range, as in the Carnot cycle.

**84. Empirical Table for Saturated Steam from 200° to 374° C.** It is easy to construct an empirical table for steam on the same lines as Table IV for  $\text{CO}_2$ , extending to the critical point. Although the values for steam in this region cannot easily be verified experimentally, the table may serve as a guide for future work and may be accepted with greater confidence on account of the experimental verification of analogous methods in the case of  $\text{CO}_2$ .

All the formulæ employed in constructing this table have already been explained and verified in the case of steam within certain limits, except that for the diameter of the density curve. This formula depends chiefly on observations of the volume of the liquid  $v$  under saturation pressure, which is fairly well established by previous experimentalists up to 320° C. Beyond this point, the author has succeeded in following the variation of  $v$  up to a temperature within 1° C. of the critical point, by heating the liquid in a series of sealed tubes of quartz-glass. The diameter of the density curve is found to be a flat parabola, and gives  $v_c = 0.521$  cb. ft./lb., or 3.25 c.c./gm. as the critical volume. The only previous measurements of the critical volume appear to be those of Nadjedine, and Battelli, giving 2.33 c.c. and 4.80 c.c. respectively, which happen to agree very closely with the values of  $v$  and  $V$  given in the table at 373° C. It is noteworthy that Nadjedine's method measured the volume of the liquid, and Battelli's that of the vapour near the critical point, so that the discrepancy between them is not surprising, considering the rapid changes of both. By combining the parabolic diameter with Clapeyron's equation, it is easy to calculate both  $V$  and  $v$  at any temperature.

The value of  $H$  reaches a maximum, 681.5, at 277° C., at which point the factor  $1 - Cdp/dt$  in equation III (7) vanishes. This gives  $C = 0.0782^\circ/\text{lb.}$  which agrees very closely with the author's curve marked  $C_8$  in Fig. 10. The same factor must vanish again at the critical point to account for the change of sign of  $dh/dt$ . This gives  $C_c = 0.0286^\circ/\text{lb.}$ , which is quite a possible value, since  $C$  for the liquid vanishes and becomes positive at 260° C. The relations of these quantities to  $S$  in the neighbourhood of the critical point have already been explained in § 80.



## le X.

Properties of Saturated Steam from 200° to 374° C. in F.P.C. units.

$t$	$p$	100 <i>v</i>	100 <i>V</i>	$L$	$h$	$H$	$G$	$\phi$	$\Phi$
200°	225.2	1.856	207.38	467.41	203.55	670.96	59.75	0.5585	1.5445
210°	256.0	1.884	170.04	459.00	214.44	673.44	65.33	0.5790	1.5291
220°	335.4	1.914	140.37	450.00	225.49	675.49	71.12	0.6015	1.5140
230°	404.5	1.946	116.67	440.60	236.71	677.31	77.11	0.6237	1.4995
240°	484.2	1.981	97.51	430.60	248.13	678.73	83.30	0.6458	1.4850
250°	575.7	2.018	81.96	420.25	259.78	680.03	89.67	0.6679	1.4713
260°	680.2	2.060	69.22	409.30	271.69	680.99	96.31	0.6903	1.4580
270°	798.6	2.106	58.69	397.56	283.89	681.45	102.98	0.7123	1.4443
280°	932.0	2.159	50.00	385.04	296.45	681.49	109.97	0.7347	1.4308
290°	1082	2.218	42.60	371.62	309.39	681.01	117.03	0.7572	1.4171
300°	1249	2.292	36.59	357.11	322.86	679.97	124.34	0.7803	1.4035
310°	1435	2.370	31.38	341.12	336.84	677.96	131.79	0.8037	1.3898
320°	1642	2.459	26.91	323.37	351.45	674.82	139.45	0.8277	1.3729
330°	1870	2.564	23.03	303.18	366.88	670.06	147.27	0.8525	1.3551
340°	2120	2.691	19.61	279.51	383.32	662.83	155.22	0.8784	1.3343
350°	2394	2.850	16.50	250.44	401.12	651.56	163.35	0.9059	1.3076
360°	2693	3.069	13.47	211.35	421.17	632.52	171.67	0.9364	1.2702
370°	3020	3.483	9.84	142.50	446.81	589.31	180.15	0.9749	1.1904
373°	3122	3.880	7.804	92.00	461.35	553.35	182.75	0.9969	1.1393
374°	3158	5.211	5.211	0	494.25	494.25	183.52	1.0474	1.0474

Formulae for the quantities in the above table:

Saturation pressure,  $\log_{10} p = 2.3526 + 4.264 (t - 200)/T$  lbs./in.<sup>2</sup> ...(*p*)Parabolic diameter,  $1/v + 1/V = 60.75 - 0.00016t^2$  lbs./cb. ft. ....(*m*)Clapeyron's equation,  $ap(V - v) = Lp/T (dp/dt) = LT/4645$  cal. C. ...(*V*)Latent heat (Thiesen),  $\log_{10} L = 1.0638 + 0.3151 \log_{10} (374 - t)$ , cal. C. (*L*)Total heat of liquid,  $h = 0.99666t + vL/(V - v)$ , cal. C. ....(*h*)Total heat of vapour,  $H = 0.99666t + VL/(V - v)$ , cal. C. ....(*H*)Gibbs' potential,  $G = 2.295 T \log_{10} T/T_0 - 0.99666t$ , cal. C. ....(*G*)Entropy of liquid,  $\phi = 2.295 \log_{10} T/T_0 + vL/T (V - v)$ , cal. C. ...( $\phi$ )Entropy of vapour,  $\Phi = 2.295 \log_{10} T/T_0 + VL/T (V - v)$ , cal. C. ....( $\Phi$ )For (*p*) see Chapter VII, equation (36), and Chapter IV, § 41.For (*L*) see Chapter II, equation (18), and Chapter IV, § 41.For (*h*) and (*H*) see Chapter II, equation (6).For ( $\phi$ ), ( $\Phi$ ), and (*G*) see Chapter VII, equations (11), (24), and (25).

Judging from the analogous case of CO<sub>2</sub> we should conclude that the formulae employed for *L* and *h* in the case of steam would be fairly satisfactory because they represent the values of *H* very closely at low temperatures (between 0° and 200° C.) which are much more accurately known than in the case of CO<sub>2</sub>. The empirical formula employed for *p* represents the observations of *p* itself within the limits of experimental error, as in the case of CO<sub>2</sub> over the corresponding range of temperature. But in the case of steam we

have the additional evidence at low temperatures, which shows that it must give far too slow a rate of change of the ratio  $(T/p)(dp/dt)$ , in this region. The same effect is observed in the case of  $\text{CO}_2$  if we compare the values of this ratio,  $1985/T$  from (1), with those given by the theoretical formula (48). It follows that the formula employed for steam in Table X must give too high values of  $p$  and  $dp/dt$  in the region between  $200^\circ$  and  $800^\circ \text{C}$ . An error of the same nature is indicated by comparison with the observations of Holborn and Baumann in Fig. 14. The effect of this is most important in deducing the values of  $V$  from those of  $dp/dt$ , which are necessarily more uncertain than those of  $p$ . This error does not affect the values of  $H$  or  $L$  appreciably, and cannot be corrected with certainty in the case of steam, because there are no satisfactory observations of the volume between  $200^\circ$  and the critical point. Even if the values of  $p$  were known with certainty, they would not suffice by themselves, as already explained, to determine a satisfactory form of the characteristic equation capable of being extended to the critical point. Even in the case of  $\text{CO}_2$ , for which the experimental data are more complete than for any other substance, this problem cannot be satisfactorily solved. In the case of steam, it would doubtless be possible to find a more probable formula for  $p$ , and to make a better estimate of the values of  $dp/dt$  and  $V$ , but since the problem is of purely theoretical interest, it would seem better to wait for more experimental evidence before proceeding to speculate on the form of the characteristic equation.

With the scanty experimental data at present available above  $200^\circ \text{C}$ ., we can hardly do more than estimate the probable limits of error of  $p$  and  $V$ . The values of  $p$  given by the empirical formula in Table X are almost certainly too high, and those of  $V$  too low as already explained. The experimental values of  $p$  in the neighbourhood of the critical point, are probably vitiated by the presence of gas, which can hardly be avoided in heating water in steel vessels at such temperatures. Holborn and Baumann succeeded in reducing this source of error by gilding the inside of the container, but they do not seem to have been able to eliminate it completely. Their results are likely to be too high, especially near the critical point, though the error from this cause would be less than that shown by the other curves in Fig. 14.

• A lower limit to the values of  $p$  can be estimated as follows. The rate of diminution of the ratio  $(T/p)(dp/dt)$  at  $200^\circ \text{C}$ . cannot well be greater than that given by the theoretical formula, VII (19).

Assuming that the ratio diminishes to a minimum 7.5, as is probable at the critical point, we find the following formula

$$(T^9/p) dp/dt = 7.5 + 7.65 (T_c - T)^2 \times 10^{-5}, \dots\dots(51)$$

agreeing with the theoretical equation, VII (19), at 200° C. The corresponding formula for  $p$ , taking  $p = 225.2$  at 200° C., and  $T_c = 647.1$ , is

$$\log_{10} p = 8.4866 - 89.54 \log_{10} (T_c/T) + 1.6615 (T_c - T) (3T_c - T) \times 10^{-5}, \dots\dots(52)$$

which gives 8066 lbs. for the critical pressure, differing by 3 per cent. from the value 3158 in Table X. The difference is no greater than that between the values given by Andrews and Amagat for the critical pressure of CO<sub>2</sub>, which would be much easier to determine than that of steam.

The value of  $p$  at 250° C., given by (52) is 567.6, as compared with 565.8 by VII (19), and 575.7 in Table X. The value of  $(T/p) dp/dt$  from (51) at 250° C. is 8.076 giving  $V = 0.850$  by Clapeyron's equation. The value of  $V$  at the same point calculated directly from II = 680.08 by III (23), with  $p = 567.6$ , is  $V = 0.886$ , as compared with  $V = 0.8695$  in Table III, App. III and  $V = 0.820$  in Table X, or  $V = 0.854$  from II with  $p = 575.7$  as in Table X.

Equation (52) for  $p$  is in some respects more probable than the empirical formula of Table X, but it is evident that a considerable margin of uncertainty must remain until further light is thrown by experiment on the form of the characteristic equation at high pressures. Since steam-pressures above 250 lbs. seldom occur in engineering practice, it hardly seems worth while to make any modifications to suit possible deviations at higher pressures from the simple formulae employed in the Steam Tables.

It is common practice to deduce the properties of steam, or other substances beyond the experimental range, from those of a similar substance (e.g. CO<sub>2</sub> which is also triatomic), by reference to the "law of corresponding states." According to Van der Waals' equation, the reduced value,  $p' = p/p_c$ , of the saturation-pressure expressed as a fraction of the critical pressure, should be the same for all substances at any given value of the reduced temperature,  $T' = T/T_c$ . Thus for CO<sub>2</sub> at -50° C., the reduced temperature  $T' = 228.1/304.6 = 0.7824$ , corresponding to a temperature  $0.7824 \times 647.1 = 473.9$  abs., or 200.9° C. for steam, at which point the pressure is 229.4 lbs. The corresponding pressures for CO<sub>2</sub>

according to equation (1), are 99.0 and 1071 lbs., at  $-50^{\circ}$  and  $+31.5^{\circ}$  C. respectively. The critical pressure for steam should therefore be  $229.4 \times 1071/99 = 2482$  lbs., which is evidently much too small. The law in this form is clearly unreliable, even for the saturation-pressures, and is much less likely to give reliable results for other properties, such as the cooling-effect, to which it has frequently been applied. According to the equation of Clausius, the law takes a slightly different form. Corresponding temperatures are those for which the reduced value of  $c$  is the same. At such temperatures the reduced values of  $p/T$  and of  $V - b$  correspond. It is always possible to satisfy the law in this form for  $p$  by choosing the variation of  $c$  to fit with that of  $p$ , but the other properties such as  $V$  and  $L$ , show little or no correspondence, as illustrated by Table VII, and the law affords no assistance for estimating the variation of  $p$  unless the variation of  $c$  can be predicted. On account of these difficulties, the application of the law has generally been abandoned except for closely related substances, but has recently been revived, on the basis of Clausius' equation, by M. Aries, in a long series of papers in the *Comptes Rendus*, 1918-19, who assumes that the variation of  $c$  with  $T$  should be the same for molecules containing the same number of atoms, recalling Maxwell's suggestion with regard to the ratio of the specific heats. The variation of  $c$  is undoubtedly different for different types of molecule, but the agreement thus obtained, except for closely related substances, is not of a sufficiently high order for the present purpose, and M. Aries finds it necessary to admit that  $b$  also is a somewhat peculiar function of the temperature. In spite of this complication, there are many notable exceptions. The variation of  $c$  which appears suitable in the case of  $\text{CO}_2$  fails entirely for steam. According to the orthodox view, the discrepancy is explained by saying that water is an abnormal, or highly associated liquid. We have seen, however, that the expressions here proposed for the total heat of water and liquid  $\text{CO}_2$  show a remarkable correspondence, and it seems more likely that the difference is due to the mode of variation of  $c$  for the vapour in either case, since different indices are required to represent the other properties satisfactorily, in addition to the saturation-pressures. In this connection, it is perhaps noteworthy that, in order to make the value of  $c - b$  for steam at  $374^{\circ}$  C. equal to the critical volume 0.0521 (which depends chiefly on the author's observations of the expansion of the liquid up to  $373^{\circ}$  C.), taking the value  $c = 0.4218$  at  $100^{\circ}$  C., it would be sufficient to assume

that  $c$  varies as  $T^{-3/2}$ , in extremely close agreement with the mode of variation required from  $0^\circ$  to  $200^\circ$  C.

It would no doubt be possible to devise an equation capable of representing the properties of steam within the limits of experimental error over the whole range  $0^\circ$  to  $374^\circ$  C., but the experimental data available in the critical region are so inadequate and uncertain that it would be impossible to discriminate satisfactorily between a variety of possible types. The problem is by no means so easy as it looks, and the solution, when found, would necessarily be very cumbrous and inconvenient for practical calculations, as compared with the simple equations which suffice for the experimental range of the steam-engine. In the case of  $\text{CO}_2$ , since the experimental range coincides with the critical region, it is impossible to avoid such complications, which otherwise would be regarded as prohibitive. But in the case of steam, it would be unreasonable to insist on the use of equations capable of representing the critical phenomena which are not required in practice.

## CHAPTER IX

### IDEAL CYCLES AND STANDARDS OF EFFICIENCY

**85. Application of the Laws of Thermodynamics to a Cycle.** The application of the laws of thermodynamics to a cycle of operations, such as are performed by a heat-engine, or can be represented on the indicator diagram, is so fully discussed in all the textbooks that a brief summary of the principal facts and formulae will be sufficient to explain the notation employed and the use of the tables in the calculation of numerical results.

**First Law.** The general expression of the first law as applied to a cycle is that the thermal equivalent  $AW$  of the work represented by the area of the indicator diagram, is equal to the difference between the heat energy  $Q'$  received by the working substance and the heat energy  $Q''$  rejected by it in the performance of the cycle, as expressed by the simple equation

$$AW = Q' - Q''. \dots\dots\dots(1)$$

**Second Law.** Since all closed cycles which can properly be represented on the indicator diagram, are reversible so far as the working substance is concerned, it follows from the second law that the entropy of the heat received is equal to the entropy of the heat rejected in any such ideal cycle.

**Symmetrical Cycles.** There are three principal types of symmetrical cycles employed in heat-engines, characterised by the reception and rejection of heat, (1) at constant temperature, (2) at constant pressure, and (3) at constant volume.

**Constant  $T$  cycle.** This is the Carnot cycle, consisting of four operations, which may be described as follows:

(1) Reception of heat energy  $Q'$  at constant temperature  $T'$ . Since  $T$  is constant  $Q' = T'(\Phi - \Phi_0)$ , where  $\Phi - \Phi_0$  is the increase of entropy.

(2) Adiabatic expansion at constant  $\Phi$  to the lower temperature  $T''$ .

(3) Rejection of heat energy  $Q'' = T''(\Phi - \Phi_0)$  at the temperature  $T''$ .

(4) Adiabatic compression at constant  $\Phi_0$  to the initial state  $T''$ .

These give the following simple and obvious relations between the change of entropy, the heat energy received, and the equivalent of the work:

$$\Phi - \Phi_0 = Q'/T' = Q''/T'' = (Q' - Q'')/(T' - T'') = AW/(T' - T''). \quad \dots\dots(2)$$

*Constant P Cycle.* This cycle comprises four symmetrical operations, similar to those of the Carnot cycle, except that heat is received and rejected at constant pressure instead of at constant temperature.

(1) The heat energy  $Q'$  received at constant pressure  $P'$  is equal to the increase of total heat  $H' - H_0'$ , where  $H_0'$  is the initial and  $H'$  the final value of  $H$  during the heating.

(2) The drop of total heat in adiabatic expansion from  $P'$  to  $P''$  at constant  $\Phi$  is denoted by  $(H' - H'')_\phi$ , but the suffix  $\phi$  may be omitted if it is otherwise obvious that adiabatic expansion is intended.

(3) The heat energy  $Q''$  abstracted at constant pressure  $P''$  is equal to the diminution of total heat  $H'' - H_0''$  required to restore the entropy to its initial value  $\Phi_0$ .

(4) The working substance is restored to its initial state by adiabatic compression at  $\Phi_0$ , during which operation the increase of total heat is  $H_0' - H_0''$ .

We thus obtain the following general expression for  $AW$

$$AW = Q' - Q'' + (H' - H'')_\phi - (H_0' - H_0'')_\phi, \quad \dots\dots(8)$$

the application of which is seen to depend on the evaluation of the heat-drop in adiabatic expansion at constant  $\Phi$ .

In the case of the steam-engine, the initial state of the fluid as supplied to the boiler by the feed-pump, is generally that of water at condenser temperature. The initial value of the total heat  $H_0'$  is that of water  $h'$ , under the saturation pressure  $p'$  of the boiler but at temperature  $T''$ . The water is heated at constant pressure, and converted into steam of total heat  $H'$ , which is adiabatically expanded from  $p'$  to  $p''$ , with heat-drop  $H' - H''$  as before. But in the third operation the steam is completely condensed to water of total heat  $h''$  at the pressure  $p''$ , by abstracting heat

$$Q'' = T''(\Phi' - \phi'').$$

The water is returned to the boiler at pressure  $p'$ , in which operation

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total heat is raised from  $h''$  to  $h'$ . Since the changes of volume and temperature in this operation are negligible, the increase  $h' - h''$  is equal to the equivalent  $av(p' - p'')$  of the work done by the feed-pump. The formula as applied to this case, becomes

$$\begin{aligned} AW &= H' - H'' - (h' - h'') = H' - H'' - av(p' - p'') \\ &= H' - h' - T''(\Phi' - \phi''), \dots\dots(4) \end{aligned}$$

which is the general formula of the Rankine cycle described in the next section.

*Constant V Cycle.* If the heat  $Q'$  is received at constant volume  $V'$ , the increase of intrinsic energy  $E' - E_0'$  during heating is equal to  $Q'$ . Similarly if heat  $Q''$  is rejected at constant volume after expansion to  $V''$ , the heat rejected is equal to  $E'' - E_0''$ , where  $E_0''$  is the final energy. If the expansion from  $E'$  to  $E''$ , and the compression from  $E_0''$  to  $E_0'$  are adiabatic, we have

$$AW = Q' - Q'' = (E' - E'')_\phi - (E_0' - E_0'')_\phi. \dots\dots(5)$$

It is possible to calculate the values of  $E''$  and  $E_0''$  from the condition of constant entropy, if the properties of the working fluid are known. The constant volume cycle corresponds closely with that employed in the internal combustion engine, where heat is communicated to the working fluid by ignition of an inflammable mixture at constant volume in the working cylinder. This method is most appropriate when air is the working fluid, but is impracticable in the case of steam, because the only convenient method of supplying heat to steam is by the use of a separate boiler at constant pressure. On the other hand, the constant pressure cycle would be very inconvenient for a gas-engine or gas-turbine, owing to the size and inefficiency of the compression pump required, and the difficulty of avoiding excessive waste of heat if external combustion were employed.

*Expression for the Efficiency.* In the case of an ideal gas, it is easy to calculate the expressions for the efficiency, which were first given by Rankine.

For the constant  $V$  cycle,  $E' - E'' = S_v(T' - T'')$ , where  $S_v$  the specific heat at constant volume, is assumed to be constant. The ratio  $T'/T''$  is  $(V''/V')^{\mu n}$ , (where  $n$  is the adiabatic index in the equation  $VT^n = K$ ), and is equal to the ratio  $T_0'/T_0''$ , of the initial and final temperatures in compression. Making these substitutions the expression for the efficiency becomes

$$AW/Q' = 1 - T''/T' = 1 - (V'/V'')^{\mu n}. \dots\dots\dots(6)$$



Similarly in the constant-pressure cycle, if the working fluid is an ideal gas with  $S_p$  constant, we have  $H' - H'' = S_p(T' - T'')$ , and the ratio  $T'/T''$  is equal to  $(P'/P'')^{1/(n+1)}$  from the adiabatic  $P/T^{n+1} = K$ . The temperature ratio in compression is the same as that in expansion, and we obtain

$$AW/Q' = 1 - T''/T' = 1 - (P''/P')^{1/(n+1)}. \dots\dots\dots(7)$$

In both cases, the expression for the efficiency in terms of the temperature range is the same as that for the Carnot cycle, provided that  $T'/T''$  is interpreted as the temperature ratio in adiabatic expansion.

If we imagine the area of the cycle on the indicator diagram divided up into a number of elementary sections by means of a family of adiabatic curves, the efficiency of each elementary section will evidently be  $1 - T'''/T''$ , where  $T'/T''$  is the temperature ratio for the section considered. The same expression for the efficiency will therefore apply to a cycle of any form for any working substance whatever provided that the ratio  $T'/T''$  is the same for all the elementary adiabatic sections into which the cycle may be divided. This condition is always satisfied in the case of the Carnot cycle for any substance, but it is satisfied in special cases only, such as that of the ideal gas, when the reception and rejection of heat are at constant pressure or volume.

When the ratio  $T'/T''$  is not the same for all the elementary adiabatic sections of the cycle, the work theoretically available must be calculated by a process of summation or integration for the elementary cycles. For each elementary cycle, if a small quantity of heat energy  $dQ$  is received at the upper limit  $T'$ , the work available is  $dQ/T'$  multiplied by the range of temperature  $T' - T''$  in the elementary section considered. The efficiency of the whole cycle is obtained by summing the available work for the elementary sections, and dividing by the whole quantity of heat energy supplied. It is always possible to perform the summation provided that the properties of the working fluid are known and that the operations of the cycle can be mathematically specified. In many cases the result can be expressed in a very simple manner in terms of the properties of the working fluid, and affords a most useful criterion of the performance of an engine working under the specified conditions, showing how much of the work theoretically available is actually realised, and indicating the directions in which improvement may be effected.

Standards in general use for this purpose are (1) the Rankine cycle for the steam-engine, and (2) the Air Standard Cycle for the internal combustion engine as recommended by the Institution of Civil Engineers\*.

**86. The Rankine Cycle.** The Carnot cycle can seldom be realised in practice, because the practical limits of working are limits of volume and pressure rather than limits of temperature. It would be very difficult to arrange for all the heat to be received by the working fluid at one temperature, especially in the case of superheated steam. In the steam-engine heat is supplied at the constant pressure of the boiler, giving a constant temperature of vaporisation, but the heat of the liquid and the superheat of the steam are supplied at different temperatures. Heat is rejected at the constant pressure of the condenser, so that the temperature of rejection is constant if the steam is saturated.\*

Rankine (*Phil. Trans. R. S. Lon.*, Jan. 1854) was the first to calculate the maximum work obtainable from a heat-engine receiving dry saturated steam at a temperature  $T'$ , and condensing the steam completely at  $T''$ . Expressed in our notation, the formula which he gave for the work obtainable per unit mass of steam was as follows

$$W = JL' (T' - T'')/T' + Js [T' - T'' - T'' \log_e (T'/T'')], \dots (8)$$

where  $J$  is the mechanical equivalent of heat,  $L'$  the latent heat of vaporisation at  $T'$ , and  $s$  the specific heat of the liquid, which is taken as constant.

The first term on the right hand side is the mechanical equivalent of the product of the entropy of vaporisation  $L'/T'$  by the range of temperature  $T' - T''$ , since the latent heat of vaporisation is all received at one temperature  $T'$ . The second term is more complicated, and represents the work obtainable from the heat supplied in heating the water from  $T''$  to  $T'$  under constant pressure, which heat is taken in by the liquid at all intermediate temperatures, ranging from  $T''$  to  $T'$ . The expression for this part of the work is obtained as follows.

If a small quantity of heat  $sdT$  is received by the liquid at any intermediate temperature  $T$ , the part convertible into work is the product of the entropy  $sdT/T$ , by the available range,  $T - T''$ , which gives the expression  $Js dT (1 - T''/T)$  for the corresponding

\* Sir D. Clerk, *Gas Engine*, vol. 1, p. 83.

element of work obtainable. The second term in the formula given by Rankine represents the integral of this expression from  $T''$  to  $T'$ , on the assumption that  $s$  is constant.

More accurately, if  $s$  is not assumed to be constant, the integral of  $s dT$  is the increase of total heat  $h$  of the liquid from  $T''$  to  $T'$  under the constant boiler pressure  $p'$ ; and the integral of  $sT'' dT/T$  is the corresponding increase of entropy multiplied by  $T''$ . This remains true however  $s$  may vary.

A similar expression for the work obtainable was subsequently given by Clausius (Poggendorff's *Annalen*, March 1856), precisely equivalent to Rankine's formula with the exception that a factor corresponding to the dryness fraction  $q$  was introduced into the first term, so as to cover the case of steam initially wet. Rankine clearly had priority of publication, so that the name "Rankine Cycle" appears to be more appropriate than the name "Clausius Cycle," which is always given to this cycle in German works, and is often found in American textbooks.

In accordance with a recommendation of a Committee of the Institution of Civil Engineers (*Proc. Inst. C. E.*, 184, Part IV, p. 284, 1898), the work obtainable in the Rankine cycle is now generally taken as a standard of comparison for the performance of steam-engines, because the Carnot cycle leads to an exaggerated idea of the possible performance, especially in the case of superheated steam.

In the formula recommended by the Committee for saturated steam, the specific heat  $s$  of the liquid was taken as unity, which is near enough for all practical purposes, though not theoretically exact. The corresponding formula recommended by the Committee for superheated steam, contains the additional term

$$JS (T_1 - T' - T'' \log_e T_1/T'),$$

which represents the work obtainable from the heat required to superheat the steam at constant pressure  $p'$  from  $T'$  to  $T_1$ , if the specific heat  $S$  of the superheated steam is taken as constant. This term is calculated in exactly the same way as the corresponding term for the liquid. The Committee proposed Regnault's value,  $S = 0.48$ , for the specific heat, but expressed a doubt as to its accuracy. As is now generally recognised, the appropriate value of  $S$  is somewhat larger and certainly variable, depending both on the pressure and on the temperature.

On account of the differences between various tables of the properties of steam, it is useful to have an authoritative formula

of this kind as a standard of reference, but in practice it is preferable to take the required values of  $H$ ,  $\Phi$ , etc. from the tables; in place of working out the Rankine formula, because this saves a great deal of trouble, besides making it possible to take consistent account of the variation of specific heat.

The expression given by Rankine tacitly assumes that the temperature of the liquid, after adiabatic compression to boiler pressure, is the same as the temperature  $T''$  of condensation. This is not exactly true, since the liquid will in general be heated by compression. In the case of water at low temperatures, the error of this assumption is quite negligible, but it may be appreciable in the case of other liquids, such as carbon dioxide, when used in the neighbourhood of the critical point for refrigeration purposes with a similar cycle.

**87. Graphic Representation of the Rankine Cycle on the  $PV$  and  $T\Phi$  Diagrams.** Many of these points are more clearly brought out when the operations of the cycle are represented on the temperature-entropy and indicator diagrams, as in the accompanying figures, which are drawn approximately to scale for carbon dioxide, because the behaviour of the liquid cannot be shown satisfactorily when the diagram is drawn to scale for water.

The curve AC in either figure is the saturation line, showing the relation between  $T$  and  $\Phi$ , or  $P$  and  $V$ , respectively, for the liquid under saturation pressure. The curve CB is the saturation line for the vapour. C is the critical point. Any point such as  $k$  inside the boundary ACB, represents a mixture of liquid and vapour in the proportion of  $dk$  to  $ck$ .

Starting from the point A, representing the state of liquid  $\text{CO}_2$  at  $0^\circ \text{C}$ ., under the saturation pressure of 500 lbs. per sq. in. abs., in either diagram, (1) the line Ab represents the adiabatic compression of the liquid to the higher limit of pressure represented by 900 lbs. The temperature is raised  $8^\circ$  in this process, and the volume is slightly diminished. (2) The line bcde represents heating at constant pressure. The part bc represents heating of the liquid to saturation temperature and volume. The part cd represents vaporisation at constant temperature  $T'$ , with absorption of latent heat  $L'$ , and increase of volume from  $v'_1$  to  $V'_1$ . The part de represents superheating of the vapour at constant pressure with a further increase of volume. The increase of total heat from b to e is represented by  $H' - h'$  in the general formula (4).

(3) The line  $efg$  represents the adiabatic expansion of the vapour, with a drop of total heat from  $H'$  to  $H''$ , corresponding to the pressure drop from  $P'$  to  $P''$ . In the  $T\Phi$  diagram,  $efg$  is a vertical straight line, because the entropy is constant. In the  $PV$  diagram, the two parts  $ef$  and  $fg$  of the curve meet at a slight angle at the point  $f$  where the adiabatic crosses the saturation line, because the form of the curve for the dry vapour is slightly different from that

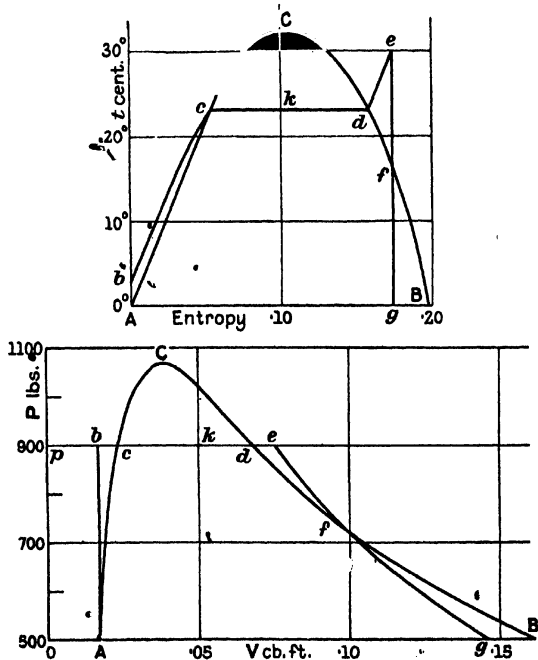


Fig. 20.  $T\Phi$  and  $PV$  Diagrams of Rankine Cycle for  $\text{CO}_2$ .

for the wet mixture. The dryness fraction  $q$  at the point  $g$  is represented by the ratio of the length  $Ag$  to the length  $AB$  in either diagram.

(4) The last operation is the condensation of the wet vapour, represented by the line  $gA$ , in which heat  $H'' - h''$  is abstracted at the lower pressure.

The area of any closed reversible cycle on the  $T\Phi$  diagram represents the heat converted into work. The corresponding closed

area on the  $PV$  diagram represents the work obtained, so that the areas are equivalent. The area of the Rankine cycle is not exactly represented by taking the saturation line  $Ac$  for the liquid in place of the broken line  $Abc$ . The difference is quite appreciable in the case of carbon dioxide, but immaterial in the case of water at low temperatures.

The work done by the feed-pump is represented by the area  $OAbp$  on the indicator diagram, which is equal to  $(P' - P'')v$ , where  $v$  is the mean volume of the liquid during compression. Even in an extreme case like that of  $CO_2$ , the area in question is very nearly a rectangle. This area is *not* represented at all on the  $T\Phi$  diagram, because the energy is supplied as work and not as heat. The whole area  $Ogep$  on the indicator diagram, to the line of zero volume, accurately represents the work-equivalent of the adiabatic heat-drop  $H' - H''$  of the vapour, being the integral of  $VdP$  from  $P''$  to  $P'$ , from which the work of the feed-pump must be deducted to get the area of the cycle. The area  $AcdefgA$  is *not* exactly equivalent to  $H' - H''$ , though this is commonly assumed in using the  $T\Phi$  diagram. The error of this assumption, represented by the area  $OAcbp$  on the  $PV$  diagram, is of the same order of magnitude as the work of the feed-pump, about 20 per cent. in the present case.

**88. The Adiabatic Heat-Drop.** The quantity most often required is the work obtainable *in the cylinder of the engine*, which is directly given by the adiabatic heat-drop  $H' - H''$ , without applying the small correction for the feed-pump work required in the case of the Rankine cycle. In any case it is important to be able to determine readily the value of the total heat  $H''$  at any point of the expansion when the entropy  $\Phi'$  remains constant. Either  $H' - H''$  or  $H''$  is directly obtained from the formula (4) already given for the Rankine cycle by transferring the small term  $h' - h''$  to the right hand side of the equation, which gives

$$H' - H'' = H' - T''\Phi' + T''\phi'' - h'' = H' - T''\Phi' + G'', \dots (9)$$

or

$$H'' = T''\Phi' - G'', \dots (10)$$

where  $G'' = T''\phi'' - h''$  by definition. Since  $G$  is the same function of the temperature for either wet steam or water, the only difficulty in applying this formula is to find the initial value of the entropy  $\Phi'$ , which necessarily depends on the data given for the initial state.

In any practical problem, it is usually necessary to find the

final value of the volume  $V''$  in addition to the total heat, but this is easily deduced from the total heat by the aid of the relations already given. The two cases of dry and wet steam will be treated separately on account of the difference of the expressions required in applying the formula, but the principle of the method is the same in both cases. The differences arise only from variations in the possible data, since the state of wet steam cannot be fixed by the pressure and temperature alone as in the case of dry steam. In many cases the final volume is given in place of the pressure or temperature, which necessitates a slight variation in the procedure.

It is sometimes necessary to distinguish between (1) the work done in *adiabatic flow*, which is the equivalent of the Heat-Drop  $H' - H''$ , and (2) the work done in *adiabatic expansion*, which is the equivalent of the Energy-Drop  $E' - E''$ , and is seldom required in practice. In a reciprocating engine, the heat-drop is the equivalent of the total work obtainable in the cylinder, and includes the work ( $P'V'$ ) done by the admission of the steam and the work ( $-P''V''$ ) done in exhausting the steam, in addition to the work of expansion  $J(E' - E'')$ . Similarly in steady flow through a turbine, the total work done is the equivalent of the Heat-Drop, and not of the Energy-Drop. The latter is so seldom required that the term expansion may be used generally to include the case of steady flow, unless otherwise specified.

**89. Adiabatic Expansion of Dry Steam.** If the final state is dry as well as the initial state, as may frequently happen in the early stages of expansion with superheated or supersaturated steam, it is often advantageous to calculate the heat-drop, or the final state, directly from the adiabatic equations, which are the same as those of a perfect gas. The advantage of this procedure is most evident when small differences are in question, as in calculating the discharge through a nozzle. The use of the tables for dry steam involves a double interpolation for both  $T$  and  $P$ , which is troublesome to perform with the necessary degree of accuracy. Whereas the adiabatic equations are extremely simple, especially if the small quantity  $b$  is neglected, as is usually done in the case of gases. The values of  $\Phi$  and  $G$  are seldom required if the initial and final states are both dry, because, if either  $P$ , or  $V$ , or  $t$ , is given for the final state, the other two are easily calculated without reference to  $\Phi$  or  $G$ . The adiabatic heat-drop is most easily found

from the formulae, given on p. 229, and in Appendix III, and the value of  $V$  is most easily calculated from that of  $H$ .

The tables are most useful for finding the initial values of  $H$ ,  $\Phi$ ,  $V$ , and  $G$ , when the range of expansion is considerable, and the final state is saturated. The value of  $H$  is the easiest to find by interpolation in the tables, since the differences are small and regular. When required below the tabulated limit of  $100^\circ \text{C}$ . for dry steam,  $H$  may easily be obtained with great accuracy from the formula,  $H = S_0 T - SCP + 464 \text{ (F.P.C.)}$ , which for purposes of numerical calculation takes the form

$$H = 594.82 + 0.4772t - P(c - 0.0037)/2.2436 \text{ (F.P.C.)} \dots (11)$$

The last term, representing  $SCP$ , being small, can be worked on a small slide-rule, with values of  $c$  from Table III (c). The small constant 0.0037 to be subtracted from  $c$ , represents  $3b/13$ ; and the factor 2.2436, representing  $3/13a$ , is the same as that required for finding  $\dot{V}$  by the formula

$$V = 2.2436 (H - B)/P + 0.0123 \text{ (F.P.C.)} \dots (12)$$

which is most often required, and is given for other systems of units in the Steam Tables, App. III. Unless small differences are in question, the initial and final values of  $H$  and  $V$  may often be obtained with sufficient approximation by reading the diagram, as explained in Appendix II.

**90. Adiabatic Expansion of Wet Steam.** The usual method of finding  $H''$  in adiabatic expansion for wet steam, is to find the final quality or dryness fraction  $q''$  from the equation of constant entropy,  $\Phi'' = \Phi'$ , or

$$\phi'' + q''L''/T'' = \phi' + q'L'/T', \dots (13)$$

and to deduce  $H''$  and  $V''$  by means of  $q''$  from the relations

$$H'' = q''L'' + h'', \quad V'' = q''V_s'' + (1 - q'')v'', \dots (14)$$

where  $V_s''$  is the tabulated volume of dry saturated steam at the final pressure.

This method involves the tabulation of the five quantities,  $v$ ,  $\phi$ ,  $h$ ,  $L$ , and  $L/T$  in addition to  $p$ ,  $t$ ,  $\Phi$ ,  $H$ , and  $V$ , and gives the required drop of total heat  $H' - H''$  as the difference between two large quantities, each of which must be carefully calculated when small differences are in question. The method is somewhat inconvenient in practice when the final volume, or the ratio of expansion, is given in place of the final pressure or temperature.



When the final volume is the given quantity it is first necessary to find the final pressure, which is generally calculated by employing Zeuner's empirical formula, namely,

$$pV^{1.035+d/10} = \text{constant} \dots \dots \dots (15)$$

This equation gives a fair qualitative representation of the adiabatics of wet steam over the range required in practice, but it is found on closer investigation that it does not agree with the tables, unless the index is taken as a function of the initial and final pressures, as well as of the wetness. Thus for steam nearly dry at 200° C., the initial value of the index is 1.155 in place of 1.185, but falls below the latter value when the range of expansion (starting at 200° C.) is extended below 100° C. The error at low pressures may amount to 15 or 20 cals. C. in the heat-drop. Many attempts have been made to express the variation of the index in terms of pressure or temperature for different ranges, but the resulting expressions are too complicated to be of much practical use. Even in its simplest shape, the formula is somewhat troublesome to work. It cannot be applied to superheated steam, and the results are often less accurate than those which may be obtained by simple inspection of a diagram (see Example 1, below).

If more exact results are required than can be obtained from a diagram the method of the next section based on the thermodynamic potential  $G$  is generally the most convenient.

*To find  $p''$  and  $v''$  if  $V''$  is given.* If the final volume is known, but not the temperature or pressure, as is the case when the ratio of expansion alone is given, the usual procedure for calculating  $q$  fails. The main object of Zeuner's equation is to meet this case by calculating the final pressure from the ratio of expansion. It is well known that Zeuner's equation does not give  $p$  very accurately from  $V$ . An exact solution, however, may easily be found by trial from the simple expression for  $V/V_s$  already given, with the aid of the tables for  $V$ ,  $H$ , and  $G$  for saturated steam. If the final volume of wet mixture  $V$  is given, the value of  $V_s$  is known approximately, since it must be a little greater than  $V$ . This gives an approximate value of the temperature, and therefore of  $H_s$  and  $G_s$  from which  $V$  may be calculated for comparison with the given value. After two trials, the exact answer can always be found by interpolation.

*Example 1.* The following example will make the procedure clear. Given  $\Phi' = 1.600$ , from the initial state, find the pressure and temperature when the steam has expanded to a volume of 200 cu. ft.

per lb. The answer can be found approximately from any diagram on which *both* volume and entropy are shown. Inspection of the diagram accompanying this book gives immediately

$$p'' = 1.87, \quad t'' = 44.5^\circ \text{C.}, \quad H'' = 505, \quad q'' = 0.807.$$

To find a more accurate solution from the tables, take as a trial solution,

$$t'' = 45^\circ, \quad V_s'' = 244.30, \quad H_s'' = 615.34, \quad G'' = 3.50, \quad H'' = 505.45.$$

This gives

$$V''/V_s'' = (505.45 - 44.85)/(615.34 - 44.85)^*,$$

or  $V'' = 197.23$ . Taking  $t'' = 44^\circ$ ,  $V_s'' = 256.45$ ,  $H_s'' = 614.88$ ,  $G'' = 3.35$ , gives  $V'' = 206.63$ . By interpolation

$$t'' = 44 + 6.63/9.40 = 44.71^\circ, \quad p'' = 1.3694, \quad G'' = 3.46.$$

Whence  $H'' = T''\Phi' - G'' = 508.48 - 3.46 = 505.02$ , which confirms the diagram. Since  $V_s''$  at  $44.71^\circ = 247.8$ ,

$$(1 - q'') = 47.8/247.8 = .1930,$$

or  $q'' = .8070$ .

It is seldom worth while, except when small differences are required, to solve problems of this kind more accurately than they can be solved by inspection of the diagram. It should be observed, however, that it is a great advantage to have both  $V$  and  $\Phi$  shown *on the same diagram*. As a rule, they are shown on different diagrams (e.g. those of Mollier) and it would be necessary to find by trial a point on the line  $\Phi = 1.60$  on one diagram giving the same state as a point on the line  $V = 200$  on the other. This is so troublesome and confusing in practice that it is generally better to use the tables, if a suitable single diagram such as that explained in Appendix II, is not available.

### 91. Use of the Potential $G$ in Adiabatic Expansion.

The thermodynamic potential  $G$  being defined by the general relation

$$G = T\Phi - H, \quad \dots\dots\dots(16)$$

the expression for the heat-drop  $H' - H''$  when  $\Phi' = \Phi''$  is evidently

$$H' - H'' = (T' - T'')\Phi' - (G' - G''), \dots\dots\dots(17)$$

which applies to any state of the steam, whether wet or dry,

\* See equation (18), next page.  $H''$  from  $G''$  by (10).

superheated or supersaturated, provided that the proper values of  $G$  are inserted in the formula. The use of this expression is most advantageous in the case of wet steam, because  $G$  is the same for water and steam in equilibrium, and its value for any mixture of water and steam is therefore independent of the composition of the mixture.

The defect of volume  $V_s'' - V''$  due to wetness is directly obtained by the equation

$$V_s'' - V'' = V_s'' (H_s'' - H'') / (H_s'' - st), \dots\dots\dots (18)$$

from the corresponding defect of total heat  $H_s'' - H''$  due to wetness, without the necessity of calculating  $q''$ . This expression is exact, according to the author's equations, and does not require any correction for the volume of the liquid or for the variation of the specific heat. The value of  $st$  is  $t - t/300$ , but it may generally be taken as  $t$  simply, since  $st$  itself is small compared with  $H$ .

The advantage of this method is that the required drop of total heat, and the required defect of volume, are directly given as small terms which may generally be calculated with a small slide-rule. The single quantity  $G$  is tabulated in place of the five quantities  $v$ ,  $h$ ,  $\phi$ ,  $\bar{L}$ , and  $L/T$ , which are so seldom required for other purposes, and are so easily calculated by the author's formulae, as not to require close tabulation. This effects a considerable simplification in the tables, and makes it possible to include all three systems of units in one table, App. III, Steam Table II, which is a matter of great convenience in comparing the results of experiments recorded in different systems of units.

Since  $G'' = T''\Phi'' - H'' = T''\Phi_s'' - H_s''$ , for wet steam, where  $\Phi_s''$  and  $H_s''$  are the tabulated values of the entropy and total heat of dry saturated steam at  $T''$ , the same formula may also be written in the convenient shape

$$H' - H'' = T'' (\Phi_s'' - \Phi') + H' - H_s'', \dots\dots\dots (19)$$

which is easy to work by taking  $\Phi_s''$  and  $H_s''$  from the tables for saturated steam in place of  $G'$  and  $G''$ . But the formula in this shape applies only when the final state is wet, and it is necessary to find  $T''$  by adding  $273.1^\circ \text{C.}$  or  $459.6^\circ \text{F.}$  to the tabulated value of  $t''$ . The results obtained will not be quite so accurate as those given by the  $G$  formula unless  $\Phi_s$  is tabulated to five places of decimals. Since  $H'$  occurs on both sides of the equation, it is evident that the formula in this shape is simply equivalent to

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$H'' = H_s'' - T'' (\Phi_s - \Phi')$ , which is obvious, and is often convenient if  $\Phi'$  is given and  $H''$  alone is required in place of  $H' - H''$ .

It was not considered worth while to tabulate  $T$  in addition to  $t$ , because the  $G$  formula for the heat-drop involves only the difference  $T' - T''$ , which is the same as  $t' - t''$ , and because  $T'$  is so easily obtained from  $t$  on the few occasions on which it is required. The potential  $G$  on the other hand is troublesome to calculate, and is worth tabulating for many other reasons.

When it is required to calculate a number of values of the heat-drop  $DH$  from a given initial state to several different final states, the formula (17) in terms of  $G$  will be found the most convenient, since  $\Phi'$  and  $G'$  are the same for each value of  $DH$  to be calculated. The work may conveniently be arranged as in the following example.

*Example 2.* Find  $DH_\Phi$  from the initial state  $P = 160$  lbs.,  $t = 200^\circ\text{C}$ ., to each of the final states,  $P = 80, 40, 20, 10, 5, 2$ , and 1 lb.

Here  $\Phi' = 1.59123$  from Table VI, and  $G' = 76.40$  from Table VII.

Final P Final t	80	40	20	10	5	2	1
	155.52	130.67	108.87	89.58	72.38	52.27	38.74
Diff. $t' - t''$	44.48	69.33	91.13	110.42	127.62	147.73	161.26
Diff. $\times (\Phi' - 1)$	26.30	40.99	53.88	65.29	75.40	87.35	95.35
Add $G''$	37.54	27.12	19.22	13.26	8.81	4.69	2.61
Subtract $G'$	- 76.40	76.40	76.40	76.40	76.40	76.40	76.40
$DH_\Phi =$	31.92	61.04	87.83	112.57	135.49	163.37	182.82

The difference  $t' - t''$  is multiplied by  $\Phi' - 1$  and added to  $t' - t''$  because this gives better accuracy with the Fuller slide-rule employed for the multiplication of  $t' - t''$  by the constant factor 0.59123. If the second formula (19) for  $DH_\Phi$ , involving the term  $T'' (\Phi_s'' - \Phi')$ , were employed for this purpose, we should have to look up  $H_s''$  and  $\Phi_s''$  in Table II in addition to  $t''$  at each point, and to find  $T''$  by adding 273.10. Both factors of the product  $T'' (\Phi_s'' - \Phi')$  would be different in each case, which would add considerably to the work required.

When on the other hand we require the heat-drop from several different initial states to the same final pressure, the second formula (19) is usually more convenient, since  $T''$  and  $\Phi_s''$  are constant; whereas both factors of the product  $(t' - t'') \Phi'$  would be different at each point in the  $G$  formula.

*Example 3.* Find  $DH_\phi$  from 160 to 1 lb., with initial temperatures  $t = 200^\circ, 250^\circ, 300^\circ, 350^\circ, 400^\circ, 450^\circ, 500^\circ$  C.  $T'' = 311.84^\circ$  C.

Initial $t$	200°	250°	300°	350°	400°	450°	500°
Initial $(\phi' - 1)$	0.59123	0.64699	0.69523	0.73810	0.77685	0.81233	0.84511
Final $(\phi'' - 1)$	0.97239	0.97239	0.97239	0.97239	0.97239	0.97239	0.97239
Diff. $(\phi'' - \phi')$	0.38116	0.32540	0.27716	0.23429	0.19554	0.16006	0.12728
Initial $H'$	676.41	704.14	730.55	756.16	781.25	806.00	830.52
$T'' (\phi'' - \phi')$	118.87	101.47	86.43	73.06	60.98	49.91	39.69
Subtract $H_\phi''$	-612.46	612.46	612.46	612.46	612.46	612.46	612.46
$DH_\phi =$	182.82	193.15	204.52	216.76	229.77	243.45	257.75

**92. Tables of Adiabatic Heat-Drop.** The adiabatic heat-drop is required as a standard of comparison for the performance of steam engines and turbines, and is often tabulated with this object, especially in relation to the efficiency required or guaranteed in commercial specifications. Tables of heat-drop in B.Th.U. based on the author's formulæ have been published\* for this particular purpose covering a range of 27 to 29 inches vacuum in tenths of an inch, with 50 to 400 lbs. initial pressure and  $0^\circ$  to  $800^\circ$  F. superheat at intervals of 10 lbs. and  $25^\circ$  F. These contain upwards of 12,000 entries, and are very complete for the required purpose; but the possible variety of initial and final states is so great, and there are so many different systems of specifying the measurement of pressure and temperature, that it would be impracticable to construct tables of this kind to meet all possible cases.

The Steam Table VIII, of heat-drop in calories Centigrade, given in Appendix III, covers a wide range of initial states, but is restricted to a final pressure of 1 lb. It will be found useful for a similar purpose, but requires the application of a vacuum correction if the final pressure differs from 1 lb. The table is arranged to correspond with Steam Tables IV, V, VI, and VII, of  $H$ ,  $V$ ,  $\Phi$ , and  $G$ , so that the initial values of these quantities are easily obtained if required in the case of superheated steam. In the case of steam below the saturation limit, the initial states are defined by the values of  $H$  given in Steam Table IV, but the initial state is taken as wet saturated instead of dry supersaturated, so that the initial values of  $V$ ,  $\Phi$ , and  $G$  are different, and must be deduced from  $H$ , if required, with the aid of Steam Table II for saturated steam. This is equivalent to supposing that the dry

\* Edward Arnold, 1917.

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supersaturated steam of Tables V, VI, and VII, is transformed into wet saturated at constant  $P$  and  $H$ , as would actually happen if the dry supersaturated steam were discharged into a receiver without loss of heat. The initial temperatures for superheated steam are those given in the column on the left; the initial temperatures for steam below the saturation limit, are the saturation temperatures given in the lowest line of the table, together with the values of the heat-drop  $DH_s$  for dry saturated steam, from the given initial pressures to a final pressure of 1 lb.

The values are tabulated to two places of decimals, in case they may be required for small differences, but owing to the number of different figures from other tables involved in the calculation of each separate result, the errors may often exceed one in the last figure of the heat-drop.

Values of the heat-drop to 1 lb., for initial pressures and temperatures intermediate between those tabulated, may generally be obtained with sufficient accuracy for most purposes by linear interpolation. But at low pressures, where the intervals are relatively large, it is sometimes advisable to employ the special rule for  $\Phi$  and  $G$  given in the Steam Tables, App. III, § 202. The largest interval (ratio  $2/3$ ) is that between 20 and 30 lbs., which is very seldom required. To find the heat-drop from 25 lbs. at  $200^\circ \text{C.}$ , by linear interpolation, we should add half the tabular difference 18.51 to 117.06, giving 123.82. By the special rule, the half-difference 6.76 should be increased in this case by  $1/10\text{th}$ , or 0.68, giving 124.50 as the correct result. The error of linear interpolation between tabulated values  $P'$  and  $P''$  can never exceed

$$(P' - P'')/4 (P' + P'')$$

of the tabular difference, e.g. between 90 and 100 lbs. the maximum error amounts to less than  $1/20\text{th}$  of a caloric, and between 450 and 500 lbs. to about  $1/30\text{th}$ . Linear interpolation for temperature difference is quite satisfactory, and may be effected simultaneously with that for pressure difference by adding the appropriate fraction of the tabular difference for  $10^\circ$ .

To correct the heat-drop to any other final temperature  $t_2$ , in place of  $t_1 = 88.74^\circ \text{C.}$ , the value for 1 lb., we have to add  $(t_1 - t_2) \Phi' - (G_1 - G_2)$ , the heat-drop from  $t_1$  to  $t_2$  at  $\Phi'$ , the initial value of the entropy. This is easier than calculating the whole heat-drop, because  $G'$  is not required, an approximate value of  $\Phi'$  suffices, and the multiplication can be done on a small slide-rule.

Thus to find the heat-drop from 25 lbs. at  $200^{\circ}\text{C.}$ , to 2 lbs. in place of 1 lb., we find  $\Phi' = 1.814$  from Table VI,  $t_2 = 52.27^{\circ}\text{C.}$ , and  $G_2 = 4.69$  from Table II, whence the required correction is  $18.58 \times 1.814 - 2.08 = 22.47$ , to be subtracted from 124.50, giving 102.03 for the heat-drop to 2 lbs. or 25.92" vacuum (Bar. 80"). But this is an extreme case. The vacuum correction seldom exceeds 10 cal.-C. The correct value of the heat-drop, directly calculated with  $\Phi' = 1.81425$ ,  $G' = 170.70$ , by 7-figure logarithms, comes out 102.02, which agrees within the probable limits of error of the tabular data.

Table VIII differs from Steam Tables IV, V, VI, and VII, by the addition of the first column for an initial pressure of 15 lbs. This has been added to include the case of low-pressure turbines, which generally work with an initial pressure between 15 and 20 lbs. The maximum error of linear interpolation between 15 and 20 lbs. cannot exceed  $1/28$  of the tabular difference, which is nearly 10 cal. at all degrees of superheat. This amounts to 0.35 per cent. of the heat-drop at the lower initial temperatures in the table, so that it may be advisable to correct the result of linear interpolation by the special rule already quoted, which takes in this case the following form.

When the given initial pressure  $P$  is intermediate between 15 and 20 lbs., find by linear interpolation the fraction  $(P - 15)/5$  of the tabular difference  $D$  at the given initial temperature, increase it by the fraction  $(20 - P)/2P$  of itself, and add the result to the tabulated heat-drop at 15.

Thus if  $P = 17$ ,  $t = 290^{\circ}$ ,  $D = 9.68$ , the correction by linear interpolation is 3.87. This must be increased by  $3/34$  of itself, or 0.84 cal. giving the result  $107.38 + 3.87 + 0.84 = 111.59$  cal. C.

The initial values of  $H$  at 15 lbs. are easily found, if required, by adding 55C to the tabulated values at 20 lbs., or half the difference for 10 lbs., namely 105C, given in the first column of Table IV. The value at the given initial pressure may be obtained with equal ease by adding the appropriate fraction of 105C, e.g. at 17 lbs. and  $200^{\circ}\text{C.}$ , add  $0.8 \times 0.884 = 0.25$  to  $H = 688.08$  at 20 lbs. Similarly, to find the initial value of the entropy, if required for the vacuum-correction, add to the tabulated value of the entropy in Table VI at 20 lbs. the fraction  $(20 - P)/5$  of 0.082, since the value of the entropy at 15 lbs. exceeds that at 20 lbs. by the nearly constant quantity 0.082, which is accurate enough for the purpose of the vacuum-correction, though not for the whole

heat-drop. The initial value of  $G$  is not required for the vacuum-correction, and that of  $V$  may be most easily obtained from  $H$  by the usual formula for dry steam.

It will be seen that most of these corrections are insignificant in practice, but they may be required if it is desired to investigate the probable effect of small changes in the initial conditions.

### 93. Absolute Thermal Efficiency of the Rankine Cycle.

The efficiency of the cycle, or the fraction of the heat received which is converted into work, is readily obtained from the expressions previously given for the work done per cycle. The heat received is the change of total heat  $H' - h'$  at constant pressure  $p'$ , from the state of water at the lower temperature to that of steam at the upper limit of superheat. The heat rejected is the product of the corresponding change of entropy  $\Phi' - \phi'$  by the temperature  $T''$ . The heat converted is  $H' - h' - T''(\Phi' - \phi')$ , which may also be put in the form  $H' - H'' - (h' - h'')$ , where  $H' - H''$  represents the work done by the steam, and  $h' - h''$  the work of the feed-pump  $Aw = av''(p' - p'')$ . We have therefore the following expressions for the efficiency  $AW/Q'$ ,

$$AW/Q' = 1 - T''(\Phi' - \phi')/(H' - h') = (H' - H'' - Aw)/(H' - h' - Aw), \quad \dots\dots(20)$$

of which the second is the most convenient for use with the tables, when combined with the formula already given for the heat-drop  $H' - H''$ .

The performance of an engine is commonly expressed in terms of the number of pounds of steam required per horse-power-hour of 1,980,000 foot-pounds (H.P.H.). The work obtainable per pound of steam in the Rankine cycle being represented by

$$1400 (H' - H'' - Aw),$$

the number of pounds of steam required per H.P.H. is given by the numerical formula,  $1414.8/(H' - H'' - Aw)$ . This is a favourite method of expression in the case of superheated steam, but is very misleading, because it obscures the fact that a pound of superheated steam contains more heat, and requires more fuel to produce it, than a pound of saturated steam. The theoretical improvement in efficiency by superheating is comparatively small even when the superheat is considerable, as shown in the following example, in which supersaturation (§ 137) is excluded.



**Example 4.** Efficiency of the Rankine Cycle for steam at 200 lbs. condensing at 40° C., with various initial temperatures.

Initial $t'$ °	$H'$	$\phi'$ °	$G'$	$H' - H''$	$AW$	$H' - h'$	Efficiency	Lbs./ H.P.H.
194.35°	669.69	1.5538	56.69	185.95	185.62	629.47	.2949	7.618 °
300°	728.82	1.6682	227.24	209.49	209.16	688.60	.3037	6.761
400°	780.26	1.7611	398.37	234.79	234.46	740.04	.3168	6.031
500°	829.93	1.8199	577.02	262.93	262.60	789.71	.3325	5.385

Final state,  $p'' = 1.0703$ ,  $G'' = 2.78$ ,  $Aw = 0.33$ ,  $h' = h'' + Aw = 40.22$ .

The calculation of the heat-drop by the formula

$$H' - H'' = (t' - t'') \Phi' - G' + G''$$

is very easy, but is not so advantageous in the case of highly superheated steam as in the case of wet steam, because the value of  $G'$  may be large, as in the last example, and the range  $t' - t''$  is also large. When the absolute thermal efficiency is required in addition to the heat-drop, it is necessary to take  $H'$  from the tables in any case, and the heat-drop may be found by the equally simple formula

$$H' - H'' = H' - T''\Phi' + G'' = H' - H_2'' + T''(\Phi_2'' - \Phi'),$$

which is just as easy to work, and saves looking up  $G'$ . The formula in terms of  $G$  is more convenient when the heat-drop is small, especially if  $H'$  is not required. The second is often preferable when the superheat is considerable, and  $H'$  is required for other purposes. See Ex. 8.

The above method of calculation is much simpler and more accurate than working out the Rankine formula with  $S_s = .48$ , and  $s = 1$ , but there is no great difference in the results if the same values of  $L$  are employed. The usual method of working out the dryness fraction  $q$  as an intermediate step with the aid of  $\phi$  and  $L/T$ , and deducing  $H''$  from  $q$ ,  $L''$ , and  $h''$ , involves more arithmetic, but is otherwise exactly equivalent to employing  $G$ , provided that  $H$  and  $h$  are defined by the same expressions.

The correction for the feed-pump work  $Aw$  is of the same order of magnitude as the effect of the variation of the specific heat. Both are generally less than errors of observation, and are unimportant for practical purposes; but neither can be exactly applied unless the relations of  $h$ ,  $\phi$ ,  $L$ , and  $H$  are defined with much greater precision than is usually attempted. The method of applying the

correction given in the above example, is that required by the author's equations and definitions. The assumption

$$h' - h'' = Aw = av''(p' - p''),$$

in adiabatic compression of the liquid from  $p''$  to  $p'$ , is very accurate, and the value of  $G''$  takes exact account of the variation of specific heat according to the formula assumed for  $h''$  under saturation pressure. The effect of the variation of  $S$  for the vapour is also exactly represented in the expressions for  $H'$ ,  $\Phi'$  and  $G'$ . But when purely empirical formulae are employed for these various quantities it is very difficult to say how the corrections should be applied or to interpret the application of the formulae in special cases. Thus if Regnault's formulae are used for  $H$  and  $h$ , it is difficult to say exactly what they mean, or to specify the variation of  $s$  and  $L$ . They have in fact been interpreted and applied in different ways with inconsistent results.

94. **The Efficiency Ratio, and the Relative Efficiency,  $F$ .** The drop of total heat in isentropic expansion, calculated by the method above explained, gives the thermal equivalent of the work theoretically obtainable under the condition of steady flow from a higher to a lower pressure, and can be calculated very accurately in any case, since it depends only on the properties of the working fluid in the initial and final states. The thermal equivalent of the work actually done by the steam in an engine or turbine for the same initial state and final pressure, must always be less than the ideal value thus calculated, provided that no additional heat is supplied after the steam has reached the engine. The ratio of the work done to the work theoretically obtainable, in the engine is a measure of the *relative efficiency* which is of greater practical utility than the absolute thermal efficiency, because it affords a fair estimate of the thermal losses due to imperfect fulfilment of the theoretical conditions.

The relative efficiency having been determined for different types of engine under various conditions by direct experiment, supplies a convenient means of estimating the performance to be expected in any given case, or the dimensions required in designing an engine for a particular purpose. But since its value cannot be determined by experiment, or predicted by theory, with a high degree of accuracy, no practical advantage is gained by insisting on small corrections, such as the work done by the feed-pump, or by distinguishing between the work done in the Rankine cycle and

the work-equivalent of the heat-drop in adiabatic expansion. The relative efficiency, denoted by  $F$ , will therefore be defined and employed in the present work as the ratio of the thermal equivalent  $AW$  of the indicated work per pound of steam to the adiabatic heat-drop  $(H' - H'')_{\phi}$  calculated from the tables, or read on the diagram, for the same initial state and final pressure. The relative efficiency thus defined is for all practical purposes the same as the ratio of the thermodynamic efficiency of the actual engine to that of the Rankine cycle, which is commonly called the "Efficiency Ratio." It is easy to allow for the difference in any case in which the accuracy of the calculations makes it worth while, but the "relative efficiency"  $F$  as here defined is the most useful quantity to employ in theoretical calculations.

It follows immediately from the above definition of the relative efficiency  $F$  that, if  $M$  is the mass-flow, or the steam supplied to the engine, in pounds per second, the indicated horse-power, I.H.P., is given by the equation

$$\begin{aligned}\text{I.H.P.} &= 2.5454MF (H' - H'')_{\phi} \text{ (F.P.C.)} \\ &= 1.4141MF (H' - H'')_{\phi} \text{ (F.P.F.)} \dots\dots\dots (21)\end{aligned}$$

The English horse-power is taken as 33,000 foot-pounds per minute at London. If the French horse-power (F.H.P.) or Cheval-Vapeur, is taken as 75 kilogrammetres per second in latitude  $45^{\circ}$ , and  $M$  is in kilograms per sec., the corresponding expression for the French horse-power in (K.M.C.) units is

$$\text{French I.H.P.} = 5.694MF (H' - H'')_{\phi} \text{ (K.M.C.)} \dots\dots (22)$$

To find the consumption of steam in pounds or kilograms per I.H.P. hour we have

$$\begin{aligned}\text{Lbs./ (I.H.P.H.)} &= 3600M / (\text{I.H.P.}) \\ &= 1414.3 / F (H' - H'')_{\phi} \text{ (F.P.C.)} \\ &= 2540 / F (H' - H'')_{\phi} \text{ (F.P.F.)} \dots\dots\dots (23) \\ \text{Kg./ (F.H.P.H.)} &= 632.3 / F (H' - H'')_{\phi} \text{ (K.M.C.)},\end{aligned}$$

which are useful for finding the value of  $F$ , when the consumption is given, by taking  $(H' - H'')_{\phi}$  from the tables or diagram for the given conditions.

By equation II (2), if there is no external loss of heat, and if the kinetic energy of the steam at release is included in the final value of  $H''$  (as would be the case if the total energy rejected were actually measured in a calorimeter), the actual heat-drop  $(H' - H'')$  will be equal to the effective heat-drop given by the

product  $F(H' - H'')$ . The effective heat-drop may be estimated from the value of  $F$  in this manner, or may be calculated from the actual heat-drop measured experimentally, by applying a correction for the external heat-loss.

In many cases the external heat-loss may be neglected, being small or less than the uncertainty of  $F$ . The actual final value of  $H''$  is thus known approximately, and the state of the steam at intermediate points of the expansion may be inferred with a fair degree of probability, or represented by a suitable curve on the diagram. This method is particularly useful in treating problems relating to nozzles and turbines, when the flow is continuous, and the intermediate states lie on a continuous curve.

Detailed examples of the applications of these and similar methods are given as illustrations of the use of the diagram, which affords ample accuracy in nearly all cases in which the relative efficiency enters, except when small differences of heat-drop are required. In the latter case it is generally necessary to use the tables, but very fair results may also be obtained by a simpler method of calculation based on the following formula.

**95. Empirical Equation for the Adiabatic of Saturated Steam.** The theoretical equation of the adiabatic, namely  $H = T\Phi_0 - G$ , is easily applied if tables of  $G$  and  $\Phi$  are available. For exact calculations in the case of saturated steam, the adiabatic drop may also be expressed in terms of  $H$  and  $T$  only, by means of the following theoretical formula

$$H' - H'' = (H' + s \times 273 \cdot 1)(1 - T''/T') + sT'' \log_e (T''/T'), \quad (24)$$

which is comparatively easy to work in the absence of any tables. But the corresponding theoretical expressions in terms of  $H$  and  $p$ , or  $p$  and  $V$  are too complicated to be of any use. For this reason an empirical expression for  $H$  in terms of  $p$  may prove useful in special cases, for obtaining the final state, or for finding intermediate points when the final state is given.

As an empirical equation for the heat-drop, it is preferable to use an equation giving  $H$  directly in terms of  $p$  or  $V$ . A suitable type of equation is the following

$$H - B' = kp^m, \quad \dots\dots\dots (25)$$

which gives an expression for the adiabatic heat-drop exactly similar to that for dry steam, except that the small constant  $b$  is omitted, and that the values of  $B'$  and  $m$  vary slightly for different

adiabatics, and are only about half as great as the corresponding constants for dry steam.

When used as a formula of interpolation, for finding intermediate values along an adiabat for which the final state is given, the values of  $k$  and  $m$  are not required in the calculation, but only that of  $B'$ , which is obtained from the simple relation

$$(H' - B')/(H'' - B') = p'V'/p''V'', \dots\dots\dots(26)$$

where  $H''$ ,  $p'$ ,  $V''$ , are the given final values. The resulting value of  $B'$  is nearly 250 for large ratios of expansion with steam initially dry. Intermediate values of  $H - B'$  are obtained from those of  $p$  by logarithmic interpolation, since  $\log(H - B')$  divides the interval between  $\log(H' - B')$  and  $\log(H'' - B')$  in the same ratio as that in which  $\log p$  divides the interval between  $\log p'$  and  $\log p''$ .

An equation of the type  $pV^\gamma = K$  is often employed for a similar purpose by calculating the appropriate value of the index  $\gamma$  to fit the initial and final states, from the relation

$$\gamma = \log(p'/p'')/\log(V''/V').$$

But it is more convenient in practice to employ this equation in the precisely equivalent form

$$pV = kp^m, \dots\dots\dots(27)$$

where  $m = 1 - 1/\gamma = \log(p'V'/p''V'')/\log(p'/p'')$ .

An equation of this type, with the appropriate value of  $m$ , fits the adiabat very closely for *small* ranges of pressure, but it has the disadvantage of being somewhat inaccurate for large ratios of expansion, and of being inconvenient for the heat-drop, which is difficult to calculate accurately from the value of  $V$  given by the formula.

The difficulty of calculation may be evaded by employing the fictitious value of the heat-drop obtained by integrating  $aVdp$ , namely,

$$H' - H'' = a(p'V' - p''V'')/m, \dots\dots\dots(28)$$

but the values of  $H$  so obtained are inconsistent with those of  $V$ , and usually lead to a discrepancy of 1 or 2 per cent. for the final heat-drop assumed in calculating  $m$ .

So much experimental work has been based on Zeuner's equation for the adiabatics of wet steam, and so many attempts have been made to find empirical expressions for the index  $\gamma$  in terms of the initial and final states and the wetness, that it is important to realise that an equation of this type cannot correctly represent the adiabat with any value of the index except for *small* ranges of

pressure. On the other hand a formula of the type (25) fits the adiabatic very fairly for large ratios of expansion, and is also useful for representing different types of expansion curves in the case of turbines, whether the efficiency is constant or varies systematically throughout the expansion.

The difference between the types of formulae here discussed is most readily appreciated by taking a specific example and drawing curves showing the difference between the theoretical values of the heat-drop and those given by the empirical methods of calculation. Curves of this kind are shown in the annexed Fig. 21 for the case of adiabatic expansion from 165 lbs. (dry sat.) to 1 lb. The abscissa in the figure represents the logarithm of the

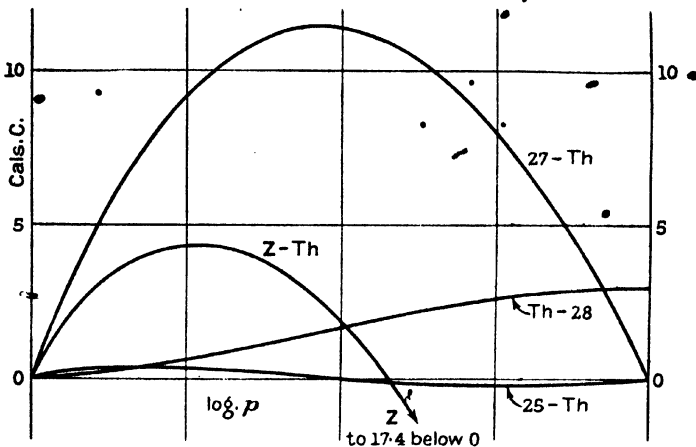


Fig. 21. Errors of Empirical Formulae for  $DH$ .

pressure-ratio; the ordinate of each curve, the difference in cal. C. of the heat-drop, as calculated by the empirical methods, from that given by the theoretical equation, represented by the horizontal base-line. The lowest curve, 25—Th, which crosses the base-line at the middle of the range, shows the excess of the values of  $H$  calculated by formula (25) over the theoretical values. The maximum error of this formula is only 0.3 of cal., or less than 1/5th of 1 per cent. of the whole heat-drop. The curve Z—Th, which also crosses the base-line near the middle, shows the deviation of Zeuner's formula (15), with the index 1.135 for dry saturated steam. This gives a positive deviation of about 5 cal., near the start, and

a negative deviation amounting to 17.4 cal. at the finish. The curve 27—Th shows the deviation of formula (27) from the theoretical when the value of the index is specially calculated to fit the final state, as is often done. The deviation then reaches a maximum of 11.5 cal. near the middle of the range. The curve Th—28, in which the sign of the difference plotted has been changed so as to bring the curve *above* the base-line, shows the effect of calculating  $m$  as in (27), but taking the heat-drop as in (28). This gives good results for small ratios of expansion, but leads to a discrepancy of 8 cal. in the final state.

Formula (25) is distinctly the most satisfactory for large ranges of pressure. If  $H''$  is given, or calculated by the theoretical formula, it is generally sufficient to take  $B' = 250$ , and the values of  $V$  at intermediate pressures may be found with sufficient approximation for most purposes by the simple formula  $V = m(H - B')/ap$ . This is less trouble than calculating  $V$  from  $H$  at each point by reference to the tables for saturated steam, but the latter method is much the most accurate.

If  $p$  is a round number given in the tables, so that no interpolation is required, it is usually more satisfactory to work a single result by means of the theoretical formula  $H = T\Phi - G$ . But if  $p$  is not a round number, and if several intermediate values are required, the empirical formula represents some advantages. Its utility becomes even more apparent if it is required to solve the *inverse problem* of finding the pressures when the division of the heat-drop is given, as in the following.

*Example 5.* Find the pressures required to give subdivision of the adiabatic heat-drop into ten equal parts from  $H = 667.55$  at 165 lbs. to  $H = 486.66$  at 1 lb.

The whole work is shown in the following table, giving the values of  $p$  at the nine intermediate points. Taking  $B' = 250$ , the values of  $H - B'$  given in the first line are obtained by successive addition of 18.089 (being one-tenth of the given heat-drop) to the final value of  $H - B'$ , namely 286.66. The second line gives the corresponding logarithms omitting the characteristic and the decimal point. The third is obtained by subtracting the logarithm (87412) of the final value from each. The values of  $\log p$  given in the fourth line are obtained by logarithmic interpolation, i.e. by multiplying each of the differences in the third line by the ratio,  $1/m = 2.2175/0.24644$  of the difference of the logarithms of the initial and final pressures to the difference of the logarithms of the corre-

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sponding values of  $H - B'$ , and adding  $\log p''$ , which in this case is 0. The theoretical values are added in the last line for comparison, as obtained by a method given in a later section.

$H - B'$	399.46	381.37	363.28	345.19	327.10	309.02	290.93	272.84	254.75
$\log H - B'$	60147	58134	56023	53806	51470	48999	46378	43590	40612
$-37412$	22735	20722	18611	16394	14058	11587	08966	06178	03200
$\log p$	2.0441	1.8633	1.6733	1.4741	1.2640	1.0418	0.8061	0.5655	0.2877
$p$	110.7	73.00	47.13	29.79	18.37	11.01	6.399	3.593	1.940
Theor.	111.3	73.56	47.53	29.97	18.41	11.00	6.368	3.567	1.927

The values of  $p$  show very fair agreement with the theoretical. It would not be at all easy to get equally accurate results from a diagram. The equal subdivision of the heat-drop on the diagram would also be a troublesome process. The graphic analogue of logarithmic interpolation is to rule a straight line joining the initial and final states plotted on logarithmic scales for both  $P$  and  $H$ . Unfortunately the scales required are so different that suitably ruled paper is unprocurable.

The formula (25) with  $B' = 250$ , is essentially one of interpolation, and would not represent the adiabatic with the same degree of accuracy unless the values of the constants  $B'$  and  $m$  were calculated to fit the final state. If the final state is not given, but only  $p''$  or  $V''$ , the formula can still be used for finding  $H$ , with certain limitations, by employing a fixed value of  $m$ , provided that the value of  $B'$  is taken to suit the initial temperature  $t'$  by the formula,  $B' = 300 - 0.27t'$ , in which case fairly accurate values of  $H$  at low pressures are given by

$$(H - B')/(H' - B') = (P/P')^{1/9} \text{ or } (V'/V)^{1/8}. \dots(29)$$

The formula in terms of  $p$  gives fairly accurate values of  $H$  with the index  $m = 1/9$ , throughout the whole range, and accurate values of  $V$  can be deduced from  $H$  by the usual formula for saturated steam. If  $V$  only is given, the formula in terms of  $V$  with the index  $m = 1/8$ , gives equally accurate values of  $H$  at low pressures, where they are most required, but is distinctly inferior to the  $p$  formula for moderate ranges, because the equation  $pV^{9/8}$  cannot fit the adiabatic throughout, and cannot be used for deducing  $p$  from  $V$ . If  $p$  is required, better values may be obtained with much less trouble from  $V$  by the formula,  $p = 1.08 (H - B')/V$ .

*Correction for Initial Wetness.* The formulae above given apply to the initial state of dry saturated steam. Zeuner's method of making the index a function of the wetness is very crude and unsatisfactory. The exact correction of the adiabatic heat-drop for



initial wetness of the steam is given in terms of the defect of  $H'$  or  $\Phi'$  by the very simple formula

$$\text{Correction of } DH_{\Phi} = (\Phi' - \Phi_s')(t' - t'') = (H' - H_s')(t' - t'')/T'', \quad \dots\dots(80)$$

where  $H_s'$  and  $\Phi_s'$  are the initial values for dry saturated steam. For this reason it is usually best to calculate the heat-drop as for dry saturated steam, and to apply the correction with a small slide-rule if the wetness is known. In a practical problem the value of  $H'$  is the quantity directly given, but if the dryness fraction  $q'$  is given in place of  $H'$ , the defect of  $H'$  may be taken as

$$H_s' - H' = (1 - q')(H_s' - t').$$

The correction for wetness is always negative, as is indicated by the sign of the term  $(H' - H_s')$  in the formula. In modern practice, the initial steam is more often superheated than wet, but wet steam is common in intermediate stages, where it is usually complicated by supersaturation.

If the initial steam is superheated, and remains superheated for an appreciable range of expansion, as is often the case in practice, an equation of the type  $PV^n = K$  cannot represent the adiabatic satisfactorily, as commonly assumed, with a single value of the index, calculated in the usual way to fit the initial and final states. The reason is that an equation of this type gives a continuous curve on the  $PV$  diagram, whereas the true adiabatic shows an abrupt change of slope at the point where it crosses the saturation line. Conversely, the curve  $PV^n = K$ , when plotted on the  $H \log P$  diagram, shows an abrupt change of slope on crossing the saturation line, whereas the true adiabatic is continuous. This follows from the fundamental relation  $dH/dP = aV$  at constant entropy, which may be regarded as the differential equation of the adiabatic.

On the other hand, a curve of the type  $H - B' = kP^m$ , satisfies the condition of continuity for  $dH/dP$ , and can be employed to represent the adiabatic with a fair degree of approximation by calculating  $B$  from the initial and final states as already explained. The approximation obtained with a single value of  $B'$  is generally within  $\frac{1}{2}$  per cent. of the whole heat-drop; but a much closer representation is secured, without any discontinuity, by using different values of  $B'$  for the superheated and saturated portions of the curve. For superheated steam the required value of  $B$  is simply 464 cal. C. (if  $b$  is neglected in the equation of the adiabatic) and the value of the index  $m$  is 3/18. At the point where the curve

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crosses the saturation line, the condition of continuity gives the simple relations

$$p(dH/dP)_s = \alpha pV_s = (8/18)(H_s - 464) = m(H_s - B'). \dots (81)$$

If  $m = 1/9$  for saturated steam, we find  $B' = 464 - (14/18)(H_s - 464)$ , which gives values of  $B'$  slightly smaller than the empirical formula  $B' = 300 - 0.27t'$ , owing chiefly to the neglect of  $b$ . The latter formula for  $B'$  is generally the most convenient and accurate. It gives  $B' = 260.3$  in the following example, in which the curve crosses the saturation line at 64 lbs., starting with steam initially superheated to  $805.67^\circ \text{C}$ . at 256 lbs.

*Example 6.* Empirical equation for adiabatic applied to superheated steam.

Pressure	256	128	64	32	16	8	4	2	1
(Theor.)	729.48	690.00	656.55	627.00	599.81	574.74	551.49	529.88	509.70
= 260.3	729.48	690.10	656.55	627.13	599.88	574.67	551.32	529.71	509.70
= 325	729.48	691.76	657.55	626.53	598.40	572.90	549.78	528.81	509.80

In the last line a single value of  $B'$  is taken throughout, and the deviations exceed 1 cal. In the second line  $B$  is taken as 464 for superheated steam, and the agreement of the empirical formula with the theoretical is seen to be extremely close.

The exact expression for the adiabatic heat-drop for dry steam in terms of the initial value of  $H$ , is readily obtained by writing the general expression for  $H$  in the form

$$H' - B = S_0 T' (1 - a(n+1)c'P'/T') + abP',$$

in which we observe that  $c'P'/T'$  is proportional to  $P/T^{n+1}$ , and is constant along an adiabatic. Thus if  $H''$  is any value of  $H$  on the same adiabatic at  $P''$  and  $T''$ , we have the simple relation

$$H'' - B - abP'' = (T''/T') (H' - B - abP'),$$

giving for the adiabatic heat-drop  $H' - H''$ , or  $DH_s$ , the expression

$$DH_s = (H' - B' - abP') (1 - T''/T') + ab(P' - P''). \dots (82)$$

The adiabatic heat-drop is obtained in terms of the pressure-ratio  $P''/P'$  by the substitution  $T''/T' = (P''/P')^{1/3}$ , since  $n+1 = 13/8$ .  $DH_s$  may also be expressed in terms of the initial value of  $V$ , by substituting for  $H'$  in terms of  $P'V'$  from the general expression for  $H$ , as follows

$$DH_s = a(n+1)P'(V' - b)(1 - (P''/P')^{1/3}) + ab(P' - P''). \dots (83)$$

When  $V$  is large, the  $b$  terms may usually be neglected in the above formulae, which then become the same in form as those applicable to perfect gases. The values of the constants in different systems of units are

$$B = 464.0, \quad ab = 0.00165, \quad 3/13a = 2.2436, \quad (\text{F.P.C.})$$

$$B = 885.2, \quad ab = 0.00165, \quad 3/13a = 1.2464, \quad (\text{F.P.F.})$$

$$B = 464.0, \quad ab = 0.0284, \quad 3/13a = 0.009847, \quad (\text{K.M.C.})$$

In working with a slide-rule it is generally best to use the reciprocal of the factor  $a(n+1)$ , namely  $3/13a$ , to reduce the number of settings.

The heat-drop for *saturated* steam, according to the empirical formula  $H - B' = kP^m$ , takes the same form as for dry steam, but with  $b$  omitted, and with the index  $1/9$  in place of  $3/13$ , thus

$$DH_\phi = (H' - B') (1 - (P''/P')^{1/9}), \dots\dots\dots(34)$$

assuming that the steam remains saturated. But it appears probable that in rapid discharge through a nozzle the steam usually becomes supersaturated, as explained in the next chapter. In this case the formulae for *dry* steam apply, with the index of  $(P''/P')$  equal to  $3/13$ , even when the initial steam is wet saturated, provided that  $DH_\phi$  is expressed in terms of  $V'$ , thus

$$DH_\phi = (13/3) aP'V' (1 - (P''/P')^{3/13}), \dots\dots\dots(35)$$

**96. Use of the Potential  $G$  in Isothermal Flow.** If the flow is isothermal instead of being isentropic, we have the condition  $T' = T''$  in place of  $\Phi' = \Phi''$ , and the expression for the drop of total heat  $H' - H''$  in terms of  $G$  becomes

$$H' - H'' = T'(\Phi' - \Phi'') + (G'' - G'). \dots\dots\dots(36)$$

Comparing this with the general expression for the drop of total heat in steady flow deduced from the first law, II (2), namely,

$$H' - H'' = Q + AW, \dots\dots\dots(37)$$

we see that the term  $T'(\Phi' - \Phi'')$  represents the heat  $Q$  abstracted per unit mass if the flow is reversible, and the term  $G'' - G'$  represents the thermal equivalent  $AW$  of the work done, including any kinetic energy generated. In other words, the increase of the potential  $G$ , as here defined, represents the external work done in reversible isothermal flow, in the same way that the drop of total heat represents the work done in adiabatic flow when  $Q = 0$ . The increase of  $G$  at constant  $T$  between any given limits of pressure

represents the thermal equivalent of the maximum work obtainable *without expenditure of fuel* per unit mass of compressed fluid, provided that the temperature can be maintained constant during expansion by communication with a large reservoir, such as the ocean, at a practically constant temperature  $T$ . The work thus obtained is equal in magnitude to the minimum work required to compress the fluid to its original state at the same constant temperature. The function  $G$  is accordingly just as useful in estimating the work done in isothermal expansion or compression, as it is in adiabatic expansion or compression. In many cases isothermal compression is more economical than adiabatic compression, and is the logical limit required in defining a standard of efficiency. The familiar refrigeration cycle is a case in point. But adiabatic compression is commonly assumed, though not the most efficient, because it is easier to calculate the work done in adiabatic compression from the tables as usually arranged. The actual compression curve is usually intermediate between the isothermal and the adiabatic, but may be considerably more efficient than the latter, if the compression is slow, especially if made in two or more stages with intermediate cooling.

97. **The Refrigeration Cycle.** The ideal refrigeration cycle is a reversed Carnot cycle in which heat  $Q''$  is abstracted from the refrigerator by the evaporation of the working fluid at a low pressure  $p''$  and temperature  $T''$ , and is transferred to the cooling water in the condenser at a higher temperature  $T'$  by the expenditure of external work  $W$  per cycle. In the ideal cycle the compression from  $p''T''$  to  $T'$  and the expansion from  $p'T'$  to  $p''T''$  are both adiabatic, but the temperature during compression is not allowed to rise above  $T'$ . The coefficient of performance, measured by the ratio of the refrigerating effect  $Q''$  to the thermal equivalent  $AW$  of the work expended in the cycle, is given, as in Carnot's cycle, by the ratio  $T''/(T' - T'')$ , and is independent of the nature or state of the working substance in the ideal case.

By employing a *mixture* of liquid and vapour throughout the cycle, it would be possible in practice to approach the theoretical condition of isothermal compression and condensation at  $T'$ , and to realise an approximation to the theoretical performance, if it were not for mechanical inefficiency of the compressor and excessive interchange of heat between the wet vapour and the walls of the cylinder.

The practical cycle more nearly resembles a reversed Rankine cycle, and is selected on the ground of simplicity of operation and convenience. The liquid is *completely* evaporated in the refrigerator at  $p''T''$ , in order to avoid evaporation by absorption of heat from the walls of the compressor, which in practice would more than counterbalance the slight theoretical gain by the compression of wet vapour. The vapour is compressed to a pressure  $P'$  slightly in excess of the saturation pressure  $p'$  corresponding to the limiting temperature  $T'$  of the condenser. During this process the dry vapour is superheated and raised to a temperature much higher than that of the condenser, so that a somewhat greater amount of work is done than would be required if the temperature were not allowed to rise above the condenser limit  $T'$ . The vapour after leaving the compressor is completely condensed, and reduced as nearly as possible to the temperature of the cooling water  $T'$ . Since very little work could be gained by the adiabatic expansion of the *liquid*, the adiabatic expansion is replaced in practice by throttling from  $P'$  to  $p''$  through a regulating valve, which effects a great simplification in the mechanism, and also in the theory, since the total heat remains constant. The refrigerating effect is the difference of total heat  $H'' - h'$  from dry saturated vapour at  $p''$  to liquid at  $P'$  and  $T'$ . The work required  $AW$  is  $H' - H''$ , the increase of  $H$  in adiabatic compression from dry saturated vapour at  $p''T''$  to  $P'$ , if the interchange of heat with the walls of the cylinder is neglected.

An example of a refrigeration cycle using  $\text{CO}_2$  is given in illustration of the use of the diagram for  $\text{CO}_2$  in the previous chapter.

## CHAPTER X

### FLOW THROUGH A NOZZLE

**98. Relation between Heat-Drop and Velocity.** The action of a turbine depends on the conversion of heat energy by flow through a nozzle into kinetic energy, which is utilised in the rotation of suitable wheels or drums provided with vanes. It is often useful to consider the conversion into kinetic energy separately from the performance of work on the revolving shaft.

It follows from the law of conservation of energy, as explained in Chapter II, section 10, that, in the case of steady flow, there is a simple relation between the heat-drop and the kinetic energy generated, since one is equivalent to the other if there is no external loss of heat. Thus if  $U$  is the velocity of steady flow at any point of a pipe or nozzle of variable cross-section, we have the relation

$$U^2 = 2Jg(H_0 - H), \dots\dots\dots(1)$$

where  $J$  is the mechanical equivalent,  $g$  the acceleration of gravity, and  $H_0$  the initial value of  $H$  when  $U = 0$ . This equation takes exact account of friction, and shows that  $H$  is the same at all points of a pipe where  $U$  has a given value. The effect of friction is to reduce the heat-drop and the kinetic energy in the same proportion. If the heat-drop is known, the value of  $U$  is found by multiplying the square root of  $H_0 - H$  by the constant  $\sqrt{2Jg}$ . The numerical values of this constant in different systems of units are independent of variations of  $g$  with latitude, etc. (provided that this is taken into account in the value of  $J$ ), and are as follows to 1 in 10,000:

$H$ in calories C.,	$U$ in feet per sec.	$(2Jg)^{1/2} = 300.2$	(F.P.C.),
$H$ in B.Th.U. F.,	$U$ in feet per sec.	$\quad \quad = 223.8$	(F.P.F.),
$H$ in calories C.,	$U$ in metres per sec.	$\quad \quad = 91.51$	(K.M.C.).

The maximum velocity attainable for a given drop of pressure is that due to the heat-drop in frictionless adiabatic expansion,

as given by the formulae in the last chapter. These formulae are especially useful in this connection, because the friction loss in a nozzle is generally small.

**99. Relation between Flow and Sectional Area.** It follows from the conservation of mass, that, when the flow is steady, the same mass  $M$  of fluid must pass every section of the pipe or nozzle per second. We have therefore the following simple relation for finding the cross-section  $X$  required to pass a flow  $M$ , at a point where the mean specific volume and velocity are  $V$  and  $U$  respectively

$$UX = kMV. \dots\dots\dots(2)$$

The value of the constant  $k$  is unity on the F.P.C. or F.P.F. systems, if  $M$  is in lbs./sec.,  $V$  in cb. ft./lb., and  $U$  in ft./sec., provided that  $X$  is measured in sq. ft. It is more usual, however, to measure  $X$  in sq. in., in which case the value of  $k$  is 144. Similarly on the K.M.C. system, if  $M$  is in kg./sec.,  $V$  in cb. m./kg., and  $U$  in metres/sec.,  $k$  is unity if  $X$  is measured in sq. m. But  $X$  is more often measured in sq. cm., in which case  $k = 10,000$ .

In most cases the required values of  $V$  are best obtained from those of  $H$ , by the usual relations for dry or wet steam. But when the steam is dry and the expansion adiabatic, the value of  $V$  may also be obtained directly from that of  $P$  by the adiabatic equation

$$P(V - b)^{1.3} = K = P_0(V_0 - b)^{1.3}. \quad p_1 v_1^{1.3} = p_0 v_0^{1.3}$$

Since  $b$  is only 1 per cent. of  $V$  for saturated steam at 800 lbs. the small terms depending on  $b$  are often beyond the limits of experimental accuracy, and may be neglected, as is usually done in dealing with gases. The adiabatic heat-drop then reduces to the form  $(18/8) a P_0^{1/3} V_0 (1 - (P/P_0)^{3/13})$ . Substituting for  $U$  and  $V$ , and putting  $\gamma$  for the adiabatic index 1.3, we find for the discharge

$$kM/X = U/V = (1/V_0)(P/P_0)^{1/\gamma} [2Jg\gamma P_0 V_0 (1 - (P/P_0)^{1-1/\gamma})/(\gamma - 1)]^{1/2}, \quad \dots\dots(3)$$

which is equivalent to the expression first deduced by de St Venant and Wantzel (*Comptes Rendus*, 1839), from Poisson's equation for the adiabatic.

But since this expression for  $M$  is somewhat complicated, and is restricted to the case of isentropic expansion with  $PP^\gamma = K$ , it is usually preferable to calculate  $U$  and  $V$  separately from the

heat-drop, and to find  $M/X$  from (2). The expression for  $U$  in terms of the heat-drop is generally true for steam or gas in any state whether the expansion is frictionless or not, provided that there is no external heat-loss.

**100. Discharge in terms of throat Area.** The discharge through a nozzle under given initial conditions is generally limited by the area of the "throat" or smallest section  $X_t$ . The condition that  $X$  is to be a minimum for a given value of  $M$ , or that  $M$  is to be a maximum for a given throat area  $X_t$ , gives  $d(X/M) = 0$ , whence  $dU/dV = U/V$ . Eliminating  $dU/dV$  by differentiating the equation  $U^2 = 2Jg(H_0 - H)$ , we obtain

$$U^2 = -JgV(dH/dV), \dots\dots\dots(4)$$

In the case of frictionless adiabatic flow, the entropy is constant, and we have  $dH = aVdP$ , or  $(dH/dV)_\phi = aV(dP/dV)_\phi$ , which gives

$$U^2/V^2 = -aJg(dP/dV)_\phi,$$

showing that the velocity in the throat is that of sound\*. Substituting for  $U/V$  from (2), we obtain the expression for the discharge

$$kM/X_t = (-aJg(dP/dV)_\phi)^{1/2}, \dots\dots\dots(5)$$

which is independent of any assumption with regard to the properties of the fluid †.

\* Holtzmann's proof (1861), quoted by Zeuner, was inadequate.

† The method employed above for deducing the velocity corresponding to the maximum mass-flow per unit area, which was first given by the author in a paper communicated to the Institution of Mechanical Engineers (*Proc. Inst. Mech. Eng.*, Feb. 1915, p. 63), has been criticised as being unnecessarily difficult and indirect as compared with the differentiation of the expression (3) given by de St Venant and Wantzel, whose method has naturally been followed in all the text-books. The maximum deduced from (3) depends on assuming the adiabatic of a perfect gas, whereas (5) has the advantage of being thermodynamically exact for all fluids, and is really more direct than the usual method, besides possessing a wider validity. Joule and Thomson (*Proc. R. S.*, 1856, p. 178) also gave an expression equivalent to (3) for the velocity of discharge of a perfect gas, and remarked that the maximum was related to the velocity of sound, but they failed to interpret the relation. Osborne Reynolds (*Phil. Mag.*, March 1886, p. 194) first showed that the velocity at the minimum area of the stream was the same as that of sound in the simple case of a perfect gas, so that, when this velocity was reached, no further lowering of pressure beyond the throat could possibly increase the discharge. His method of finding the critical velocity, involving 12 equations applying only to the perfect gas, is unnecessarily circuitous, and he expressly states that his reasoning does not apply to the case of a liquid. Whereas the author's method shows that the identity of the critical throat-velocity with that of sound applies equally to all



If we assume an adiabatic equation of the type  $P(V-b)^\gamma = \text{constant}$ , we find

$$kM/X_t = \sqrt{aJg\gamma P_t/(V_t - b)}, \quad \dots\dots\dots(6)$$

which applies to the case of dry steam if  $\gamma = 1.80$ , and is the exact expression for the discharge in terms of  $P_t$  and  $V_t$  in the throat.

Since  $b$  is very small, the expression for the throat velocity, namely,

$$U_t^2 = aJg\gamma PV^2/(V-b), \quad \dots\dots\dots(7)$$

may be simplified by neglecting terms involving  $(b/V)^2$ , which gives

$$U_t^2 = aJg\gamma P(V+b). \quad \dots\dots\dots(8)$$

Substituting this expression in the equation  $U^2 = 2Jg(H_0 - H)$ , neglecting  $(b/V)^2$  and higher orders, and eliminating either  $P$  or  $V$  as required by the aid of the adiabatic equation, we have the following equations for  $H_t$ ,  $P_t$ , and  $V_t$ :

$$H_0 - H_t = (\gamma - 1)(H_0 - B)/(\gamma + 1) + abP_t, \quad \dots\dots\dots(9)$$

$$P_t/P_0 = [2/(\gamma + 1)]^{\gamma/(\gamma-1)}(1 + b/V_0 - 2b/V_t), \quad \dots\dots\dots(10)$$

$$V_t/V_0 = [(\gamma + 1)/2]^{1/(\gamma-1)}(1 + (\gamma + 2)b/\gamma V_t - (\gamma + 1)b/\gamma V_0), \quad \dots\dots\dots(11)$$

which apply for any value of  $\gamma$ , and may be reduced to correspond with the usual formula  $PV^\gamma = \text{constant}$ , by simply omitting the  $b$  terms.

**101. Numerical Formulae for Steam.** The general formulae above given may be applied to any gas or vapour by employing the appropriate values of the constants,  $a$ ,  $b$ ,  $\gamma$ , and  $B$ , and substituting the approximate values of  $P_t$  and  $V_t$  in the small terms.

In the case of dry steam, putting  $\gamma = 1.80$ , they become

$$(H_0 - H_t)/(H_0 - B) = 0.18042 + 0.126b/V_0, \quad \dots\dots\dots(12)$$

$$P_t/P_0 = 0.5457 - 0.189b/V_0, \quad \dots\dots\dots(13)$$

$$V_t/V_0 = 1.5984 - 0.281b/V_0. \quad \dots\dots\dots(14)$$

Since these formulae involve ratios only, they are independent of the system of units adopted, provided that the proper values of  $B$  and  $b$  are employed.

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fluids, whatever their properties. But since, in the case of water, the production of the critical velocity requires a head more than 70 miles high, the effect in question could seldom be observed, and is of little practical importance in the flow of water, though undoubtedly true for liquids, as well as for gases and vapours in any state.

Substituting the values of  $P_t$  and  $V_t$  in the expression for the discharge we find

$$kM/X_t = 0.5852 (\alpha \gamma J g P_0/V_0)^{1/2} (1 + 0.274b/V_0), \dots (15)$$

which gives for the discharge in pounds per second per square inch of throat, when  $P_0$  is in lbs. per sq. in. abs., and  $V_0$  in cubic feet per lb.,

$$M/X_t = 0.3155 (1 + 0.274b/V_0) (P_0/V_0)^{1/2} \text{ (F.P.C. or F.)}, \dots (16)$$

or in kilograms per second per square centimetre, when  $P_0$  is in kg. per sq. cm. and  $V_0$  in cubic metres per kg.,

$$M/X_t = 0.02090 (1 + 0.274b/V_0) (P_0/V_0)^{1/2} \text{ (K.M.C.)}, \dots (17)$$

For steam initially dry and saturated, the discharge may be expressed in terms of  $P_0$  alone by substituting for  $V_0$  from the empirical equation,  $P_0 V_0^{16/15} = 490$  (F.P.C. or F.), or 1.786 (K.M.C.), which gives the formulae

$$M/X_t = 0.01730 P_0^{31/32} \text{ (F.P.C. or F.)}, \dots (18)$$

$$M/X_t = 0.01593 P_0^{31/32} \text{ (K.M.C.)}, \dots (19)$$

but these formulae, though simple in appearance, are not so accurate as those given above, and are not so easily applied when tables of  $V$  are available, because it is much easier to work  $(P_0/V_0)^{1/2}$  on a slide-rule than to find  $P_0^{31/32}$ . The small term  $0.274b/V_0$  is omitted in these formulae, because it is only 0.274 per cent. at  $P_0 = 300$  lbs., and is beyond the limit of accuracy of the empirical formula  $PV^{16/15} = 490$  for saturated steam.

In the case of dry saturated steam, to which the formula  $PV^\gamma = \text{constant}$  is generally applied, it is usual to take the value of the index  $\gamma$  as 1.185, from Zeuner's empirical formula, which gives the equations

$$P_t/P_0 = 0.5770, \quad V_t/V_0 = 1.6225, \dots (20)$$

$$M/X_t = 0.3003 (P_0/V_0)^{1/2} = 0.01646 P_0^{31/32} \text{ (F.P.F. or C.)}, \dots (21)$$

$$M/X_t = 0.01990 (P_0/V_0)^{1/2} = 0.01516 P_0^{31/32} \text{ (K.M.C.)}, \dots (22)$$

which are 5 per cent. smaller than the values above given for dry steam.

The theoretical objections to these formulae are, (1) that Zeuner's empirical formula does not agree exactly with the tables for wet steam, and (2) that no appreciable condensation can occur in the time taken to reach the throat, which is generally of the order of

one two-thousandth part of a second. The practical objections are, (1) that these formulae do not apply to superheated steam, and (2) that, in the case of saturated steam, they give values which are almost invariably too small, in spite of friction, and cannot be reconciled with the results of experiment. This point has been more fully discussed by the author in the *Proc. Inst. Mech. Eng.*, Feb. 1915, pp. 58-77.

**102. Effect of Supersaturation.** In the case of dry saturated steam, better agreement with experiment is obtained if we assume that the steam, on account of rapid expansion, is always supersaturated in the throat of a nozzle. The discharge of saturated steam is then determined by the same equations as for superheated steam with the index  $\gamma = 1.80$ . For steam initially wet, the same formula gives the theoretical limit of the discharge, since evaporation of the suspended water drops, or condensation on suspended nuclei, would be comparatively slow in the early stages of supersaturation. In each case the actual initial volume of the steam  $V_0$ , whether wet, or saturated, or superheated, must be inserted in the formula. The required value of  $V_0$  can be obtained from the tables, or by inspection of the diagram.

With steam at an initial pressure  $P_0 = 100$  lbs. abs., the drop of temperature to the throat, if the condensation were able to keep pace exactly with the expansion according to the usual equation, for wet steam, would be only  $20.7^\circ \text{C}$ . But, if there is no condensation, the drop of temperature found for steam in the supersaturated state is  $57^\circ \text{C}$ . The density of the supersaturated steam at this stage is about three times the density of saturated steam at the same temperature. The ratio of the density or the pressure to the saturation value at the same temperature may be taken as a measure of the supersaturation. The ratio of expansion to the throat, according to equation (20), is only 1.6, the degree of supersaturation at this stage is comparatively slight, and the condensation relatively slow. But, if we supposed the state of supersaturation to continue until the pressure had fallen to a tenth of its initial value, corresponding to a ratio of expansion 5.9, the temperature would be  $20^\circ \text{C}$ . below zero, and the density would be about a thousand times the saturation value at this temperature. We have no experimental knowledge of the rate of condensation under such conditions, but it must evidently be extremely rapid. Since a relatively small change (1.6 to 5.9) in the expansion ratio makes so

great a change (8 to 1000 times) in the supersaturation, we should infer that the limit of expansion at which condensation begins, would be very sharply marked.

Lord Kelvin (*Phil. Mag.*, 1870) showed that the vapour pressure  $p$  in a fog containing drops of radius  $r$ , was given by the equation

$$RT \log_e (p/p_0) = 2Yv/r, \dots\dots\dots(28)$$

where  $p_0$  is the normal vapour pressure at the temperature  $T$ , and  $Y$  is the surface tension of the liquid of specific volume  $v$ . The ratio  $p/p_0$  is the measure of the supersaturation. According to this equation, the radius of a drop in equilibrium with the vapour at  $20^\circ$  C. when the supersaturation  $p/p_0 = 8$ , should be  $5 \times 10^{-8}$  cm., which is something approaching molecular dimensions.

C. T. R. Wilson (*Phil. Trans.*, 1897) has shown that water vapour mixed with air at  $20^\circ$  C., in the absence of dust or other nuclei, can be expanded until its pressure is eight times that of saturation without any condensation occurring; but that, if this limit be exceeded, condensation takes the form of an excessively thick fog of very fine particles, as though the vapour itself contained innumerable nuclei capable of acting as centres of condensation. It seems probable that these nuclei are the coaggregated molecules (required for explaining the deviations of the vapour from the laws of gases) which are larger than the single molecules, and are capable of starting the condensation when the supersaturation reaches this limit. The condensation, once started, will be extremely rapid, owing to the enormous number of nuclei available, about  $10^{22}$  per lb. at  $20^\circ$  C.

For steam initially saturated, expanding according to the law  $PV^{1.3} = K$ , the limit of the supersaturated state is reached when the pressure has fallen to about one-third of the initial value. The exact pressure at which condensation begins cannot be determined with certainty, but is immaterial for the present purpose. The important point to observe is that there will be no appreciable condensation in the throat, so that the mass discharge is determined by the equation for dry or supersaturated steam. But that soon after passing the throat, the condensation will be extremely rapid, so that the remainder of the flow in an expanding nozzle approximates more nearly to that given by the adiabatics of wet steam. Thus for steam initially dry and saturated at 100 lbs. abs. the throat pressure will be 54.6 lbs., and the discharge 1.50 lbs. per sec. per sq. in. of throat. Condensation will begin when the pressure

has fallen to about 35 lbs., and the temperature from  $164.8^{\circ}\text{C}$ . to  $70^{\circ}\text{C}$ . The saturation pressure at  $70^{\circ}\text{C}$ . being 4.52 lbs. is about an eighth of the actual pressure, namely 35 lbs. At this pressure we may suppose, in order to simplify the calculation, that the steam is instantaneously transformed at constant total heat  $H = 619.2$ , into wet steam at saturation temperature (say  $T = 400^{\circ}\text{C}$ .),  $t = 126.25^{\circ}\text{C}$ . If the steam had expanded reversibly in the wet state from 100 to 35 lbs., its total heat would have been  $H_g = 616.8$ , which is 2.4 less than the value 619.2. The condensation involves an increase of entropy  $2.4/400$ , from 1.6082 to 1.6142, because the change from the unstable state of supersaturation to the equilibrium state of wet steam is an irreversible process. The expansion may then be supposed to continue, following the adiabatic  $\Phi = 1.6142$  for wet steam. The exact point at which the change is supposed to occur makes very little difference, because it affects only the small change of entropy. In point of fact the change would be continuous, since it involves an increase of 16 per cent. in the volume, from 9.962 (supersaturated) to 11.210 (wet). Some supersaturation would still persist at lower pressures, because the condensation cannot maintain exact equilibrium when the expansion is so rapid. This would tend to raise the entropy still further, so that the wet adiabatic 1.6142, represents the limit of possible performance. In consequence of the increase of entropy, the volume at any given pressure will be slightly greater than it would have been if the steam had followed the wet adiabatic from the saturation point. The change of path may be more readily appreciated by reference to the diagram, in a later section.

### 103. Example of Discharge of Supersaturated Steam.

The following table illustrates the relation between the cross-section of a nozzle and the pressure of the expanding fluid at any point, as calculated for various cases by the method explained in the previous section.

The values of  $X/X_0$ , calculated from the usual type of equation  $PV^\gamma = K$ , depend only on the ratio  $P/P_0$ , but those for actual steam depend to some extent on the absolute value of  $P_0$ . It is therefore impossible to give an exact table of ideal values to suit all cases, but in practice it is sufficient to calculate the final area to suit the final pressure, and connect it to the throat by any smooth contour having a sufficiently small angle of divergence to secure stream line flow as nearly as is practically possible.

Table I. Ratio  $X/X_i$  in terms of  $P/P_0$  for various cases.

$P/P_0$ per cent.	For perfect gas with index			For steam with $P_0 = 100$ lb.		
	$\gamma = 1.40$	$\gamma = 1.30$	$\gamma = 1.1304$	From tables	Super- saturated	With friction
90	1.620	1.586	1.523	1.530	1.588	1.565
80	1.221	1.201	1.165	1.172	1.202	1.199
70	1.073	1.061	1.041	1.042	1.062	1.053
60	1.012	1.007	1.001	1.002	1.007	1.004
50	1.002	1.005	1.015	1.014	1.005	1.008
40	1.038	1.051	1.083	1.080	1.051	1.062
30	1.134	1.162	1.228	1.224	1.320	1.337
20	1.346	1.403	1.538	1.533	1.642	1.684
10	1.931	2.075	2.420	2.418	2.576	2.699
5	2.900	3.214	3.992	4.009	4.255	4.564
2	5.159	5.959	8.052	8.158	8.660	9.580
1	8.116	9.680	13.957	14.338	15.175	17.210
$X_i$ in sq. in. for $M = 1$ lb. per sec.				0.700	0.668	0.679

The values given in the column headed  $\gamma = 1.40$  would represent the case of a nozzle for expanding compressed air. In the absence of friction or pre-heating, the temperature would fall below the liquefying point of air, when the pressure was reduced to 1 per cent. of its initial value. The values in the column  $\gamma = 1.30$  similarly represent the case of steam when sufficiently superheated to prevent condensation. The value of the index  $\gamma = 1.1304$  represents very closely the case of steam initially dry and saturated at a pressure of 100 lbs. per square inch abs., on the assumption that the condensation is able to keep pace exactly with the expansion, so that the temperature of the steam is always that of saturation corresponding with the pressure. The values calculated from the Tables for steam in this initial state are given in the next column, and show a very close agreement from 100 to 10 lb. pressure, because the value of the index 1.1304 was selected to fit this case. For lower pressures the actual expansion of the steam is rather larger than that given by the index 1.1304.

The primary effect of supersaturation is to increase the discharge by about 5 per cent. for a given throat area as compared with that usually calculated for saturated steam. The secondary effect is to cause an increase of entropy and volume after passing the throat when the steam becomes wet. The two effects taken together require, for a given throat area and ratio of initial to final pressure, an increase of 6 to 8 per cent. in the final area of the

divergent cone, or an increase of length of 8 to 4 per cent. for a given angle of divergence.

**104. Method of Calculation, including Friction.** The following table shows the method of calculation, in F.P.C. units.

Table II.

Section calculated for supersaturated steam					Corrected for friction			
<i>P</i>	<i>H</i> <sub>0</sub> - <i>H</i>	<i>U</i>	<i>V</i>	<i>X/M</i>	<i>H</i> <sub>0</sub> - <i>H</i>	<i>U</i>	<i>V</i>	<i>X/M</i>
90	4.76	655	4.826	1.061	4.74	654	4.826	1.063
80	9.95	947	5.281	.803	9.85	942	5.284	.808
70	15.67	1188	5.851	.709	15.42	1179	5.858	.716
60	22.04	1410	6.588	.673	21.55	1394	6.604	.682
Throat	25.90	1528	7.088	.668	25.22	1508	7.114	.679
50	29.31	1625	7.575	.671	28.44	1601	7.613	.685
40	37.77	1845	8.991	.702	36.34	1810	9.070	.722
30	48.79	2097	12.84	.882	46.41	2045	12.90	.908
20	64.47	2411	18.37	1.097	60.32	2332	18.53	1.144
10	89.65	2843	33.97	1.721	81.61	2712	34.54	1.834
5	112.97	3191	63.01	2.843	100.2	3005	64.71	3.101
2	141.31	3570	143.4	5.785	121.4	3308	149.5	6.51
1	161.08	3810	268.3	10.141	135.1	3490	283.3	11.69

The value of the heat-drop  $H_0 - H$  for supersaturated steam may be calculated directly from the adiabatic equation, IX (32), which is practically the same as that for a perfect gas. This method is equivalent to first finding  $T$  from the adiabatic  $P/T^{3/5} = K$ , and deducing  $H$  from the general expression IX (11), or Table IV, App. III. But it is less trouble in practice to find  $t$  by interpolation from the  $\Phi$ -table for supersaturated steam. Thus if  $P_0 = 100$ ,  $H_0 = 661.82$ , and  $\Phi_0 = 1.6082$  (Table II), we find  $t = 99.60^\circ$  at  $P = 50$  in Table VI. The corresponding value of  $H$  from Table IV for supersaturated steam is found by interpolation to be 632.51, whence  $H_0 - H = 29.31$ , the value required. The velocity  $U$  is found from the formula  $U = 300.2 (29.31)^{1/2} = 1625$ . The volume  $V$  is found from  $H$  and  $P$  by the formula for dry steam giving  $V = 7.575$ , whence

$$X/M = 144 V/U = 0.671. \quad \circ$$

For pressures below 85 lbs. (assuming instantaneous conversion) the tables for saturated steam are employed, with the corresponding formula for the heat-drop, substituting  $\Phi_0 = 1.6142$  as already explained, and the corresponding values of  $t_0 = 126.25^\circ$ ,  $H_0 = 619.2$ ,  $G_0 = 25.48$  ( $H_0 = 619.2$  is the value for supersaturated steam at 85 lbs., and the value of  $\Phi_0$  for the wet steam at the same  $H$  and  $P$

is given by  $(H + G)/T = 1.6142$ .  $V$  is found from  $H$  by the formula for wet steam.  $U$  is given by the heat-drop reckoned from the initial state  $H_0 = 661.82$ , and  $X/M$  follows as before.

The effect of friction must always be to increase the entropy and diminish the available heat-drop for any given limits of pressure. This involves a diminution of velocity and an increase of volume (as compared with the values calculated for frictionless flow), both of which tend to diminish  $M/X$ , i.e. to diminish the discharge for a given area or to increase the sectional area required for a given discharge.

The effect of friction in the throat on the discharge for a given throat area, can be estimated by employing the nozzle as a simple throttle, and observing the loss of pressure and of available heat-drop for small pressure differences as the discharge approaches a maximum. For a convergent-divergent nozzle with a stream-line contour, it is possible to raise the back-pressure considerably above the throat pressure without appreciably affecting the discharge or the velocity in the neighbourhood of the throat. The initial and final velocities being small, the actual heat-drop is small, and is readily estimated by observing the initial and final conditions. The defect of heat-drop from that due to the pressure difference in frictionless flow, is an approximate measure of the throat friction, provided that due allowance is made for any heat losses. The best form of contour for the throat may be determined by experiments of this kind. There are few satisfactory observations available, but it appears that the order of magnitude of the throat friction may be approximately represented, for a short stream-line nozzle, by a fractional reduction of the heat-drop given by the formula  $1/P_0 D$ , where  $P_0$  is the initial pressure in lbs. per sq. in. and  $D$  is the throat diameter in inches. This amounts to 1 per cent. for 1 in. diam. at 100 lbs. abs., and appears to be of the right order of magnitude to account for the defect of the observed discharge from the theoretical formula for supersaturated steam.

Friction beyond the throat will not appreciably affect the discharge, but tends to increase the sectional area required for a given final pressure. The amount of such friction in an expanding nozzle is at present a somewhat uncertain quantity owing to lack of experimental data. Assuming that it varies as the square of the velocity, or directly as the heat-drop, the loss of heat-drop due to friction would be represented by a percentage proportional to the heat-drop itself. This is the simplest assumption that can be made,



and appears to accord fairly with the scanty and imperfect data available.

The values given in the last column of the preceding table as including friction, are calculated on this assumption in the following manner. The theoretical limiting values of the heat-drop for the case of supersaturation with  $P_0 = 100$  lbs. are first calculated according to the method already given. The corresponding values of  $V$  and  $U$  give  $M/X$  at each point, from which the ratios  $X/X_t$  are obtained, as given in the column headed "Supersaturated." To make an approximate allowance for friction in a typical case, the throat friction is taken as 2.5 per cent. of the heat-drop to the throat calculated by equation (12), namely,

$$H_0 - H_t = (.18642 + .00045) (661.82 - 464.0) = 25.90 \text{ cal. C.}$$

According to the formula  $(H_0 - H_t)/P_0 D$  for the throat friction as a fraction of the heat-drop, this is equivalent to taking the throat diameter  $D$  as 1 cm. or  $\frac{1}{4}$  inch. The *percentage* reduction due to friction in this case is one-tenth of the heat-drop. All the other values of the heat-drop are accordingly reduced by a percentage equal to one-tenth of the heat-drop in calories at each point. This gives a reduction of 9 per cent. in the heat-drop at 10 lbs. and 16 per cent. at 1 lb.—values which are within the range of possibility for a nozzle of this size with so large a ratio of expansion. The values of  $U$  and  $V$  are then calculated from the reduced values of the heat-drop, and the ratios  $X/X_t$  found as before.

The effect of friction in the expanding portion of the nozzle should evidently be roughly proportional to the length of the nozzle, other conditions being equal. The friction may therefore be reduced by diminishing the length or increasing the angle of divergence. Increase of length, on the other hand, with reduction of angle, gives a more effective stream-line flow, and also diminishes the loss due to supersaturation by allowing more time for the steam to condense. Experiments on these points are wanting, but it appears that the dimensions selected in practice represent an empirical compromise between these opposite effects. It should be observed, however, that the usual method of calculating the final sectional area for a given pressure neglects both friction and supersaturation, and may give results 20 per cent. too small. This would perhaps explain the common observation that a nozzle generally "works better when the final pressure is somewhat higher than that for which it was designed. The effects of friction and supersaturation

are too large to neglect in the design, and further experiments on these points are desirable.

### 105. Variation of Discharge with Initial Temperature.

Additional evidence with regard to the law of the discharge may be obtained by taking observations at the same pressures, but at different initial temperatures. As an illustration we may apply the theory of supersaturation to explain some results quoted by Prof. Mellanby (*Proc. Inst. Mech. Eng.*, Feb. 1913, p. 295), in which

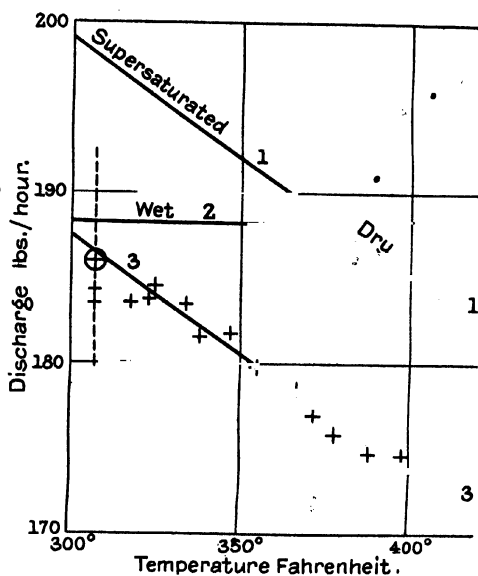


Fig. 22. Variation of Discharge with Temperature.

the discharge through a nozzle  $\frac{1}{4}$  inch diameter and  $\frac{1}{2}$  inch long, with a rounded entrance of  $\frac{1}{4}$  inch radius, at an inlet pressure of 74.2 lbs. and back-pressure 41.5 lbs. abs., was measured by means of a surface condenser, at various degrees of initial superheat. The observed values of the discharge in lbs. per hour are plotted on a large scale against the initial temperature Fahrenheit in the accompanying Fig. 22, the observations being represented by crosses. The result found with dry saturated steam at 306.8° F. is shown by the cross enclosed in a circle at 188.0 lbs. The value of the discharge at this point calculated by the usual formula for wet steam is 188.4,

whereas the formula for supersaturated steam gives 199.0 lbs. This result would appear at first sight to justify the usual formula, except that the coefficient of discharge is surprisingly close to unity for so small a nozzle with so long a throat. Prof. Mellanby found however a coefficient of discharge *greater than unity* with a shorter nozzle of the same size, but suggested that the discrepancy might be due to the wetness of the steam, or the errors of the steam tables, rather than to any defect in the theory. But his results at higher temperatures do not support this explanation.

According to the usual theory of reversible condensation, the maximum discharge as calculated from the tables should remain nearly constant (in this case) and equal to 188.2 lbs. per hour until the initial temperature is raised to 377° F. (at which point the steam would be just saturated on reaching the throat) as shown by the nearly horizontal line 2 for steam which is wet on reaching the throat. When the superheat is increased beyond this point, the discharge should fall off as shown by the curve 1 for dry or supersaturated steam. The observations however do not follow a broken curve of this type, but are very closely represented by line 3, which is obtained by simply reducing the curve 1 for supersaturated steam by 6 per cent. This reduction may reasonably be attributed to friction in so small a nozzle, and the *form* of the curve may be regarded as conclusive evidence in favour of the theory of supersaturation, since there is no indication of any well marked break.

**106. On the Supersaturation Limit.** The existence of the loss due to supersaturation in the rapid expansion of steam, appears to have first been pointed out by Prof. Nicolson and the author in a paper "On the Law of Condensation of Steam" (*Proc. Inst. C. E.*, 1898, pp. 22-30) as a necessary consequence of the finite rate of condensation shown by their experiments. They estimated that a drop of 50° F. below saturation, corresponding to a missing quantity of 5 or 10 per cent., might be expected under ordinary conditions in a high-speed engine. By measuring the temperature of the steam during expansion with a compensated platinum thermometer (Fig. 7) of very fine wire, they found that the observed temperature was always lower than that deduced from the indicator. But they pointed out that any thermometer, however sensitive, could be expected to indicate a small fraction *only* of the fall of steam-temperature, because the condensation on its surface would tend to keep it at the saturation point. By measuring

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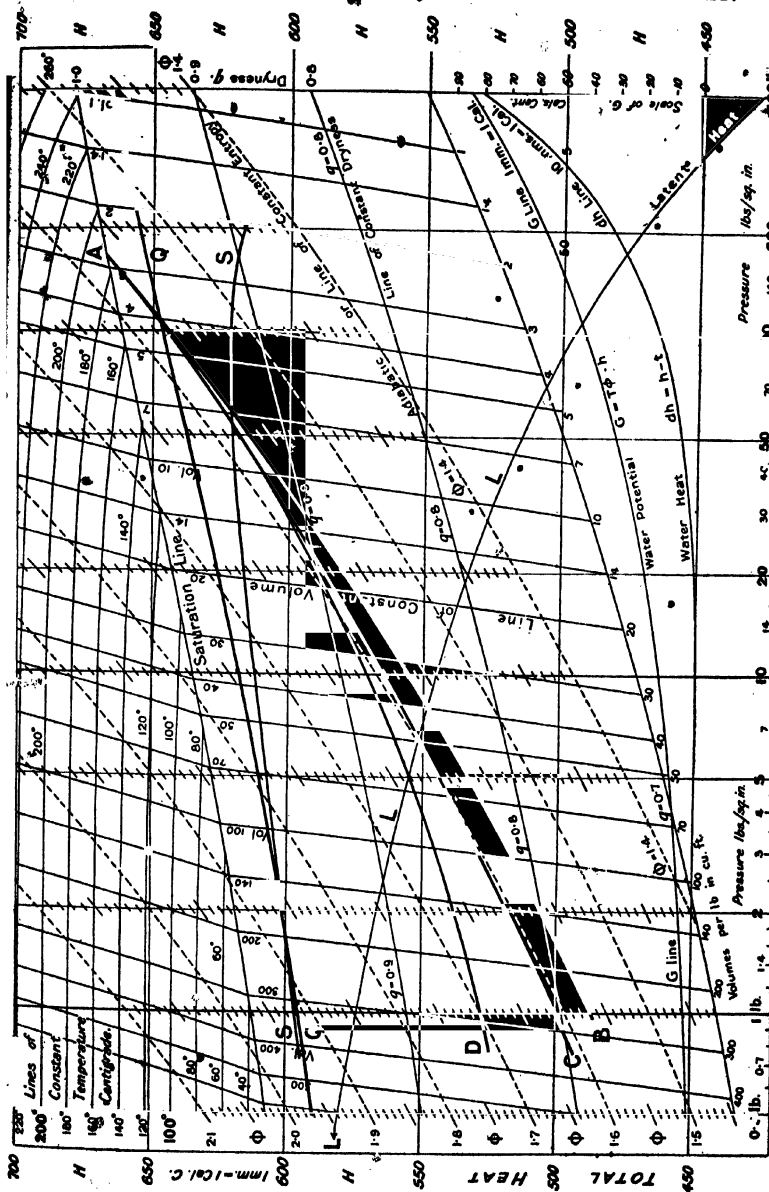


Fig. 23. Adiabatic AC for Steam at the Supersaturation Limit SS on the H log P diagram.

the adiabatic index, for dry steam with a thermometer of the same type, they inferred that the loss of work, if there were no condensation, might amount to 20 per cent. for large ratios of expansion. But this was regarded as an overestimate, because there was known to be a *limit*, although Wilson's experiments, which first afforded a direct determination of the limit in the case of moist air at ordinary temperatures, had not been published at the time when the paper was written. The difference is readily appreciated by reference to the curves shown on the diagram (Fig. 28). The curve AB represents the adiabatic for saturated steam, the curve AD that for dry steam, expanding from 165 lbs. to 1 lb. without condensation. This shows a defect of heat-drop amounting to 20 per cent. at 1 lb. The curve SS shows the supersaturation limit, drawn on the hypothesis that condensation begins very rapidly when the pressure is eight times the normal saturation pressure corresponding to the temperature. If the temperature of the steam cannot fall below this limit, the adiabatic for supersaturated steam AC will begin to diverge from the dry adiabatic AD at the point where it crosses the curve SS, and the later part of the supersaturation curve will approximate more closely to AB than to AD. Since AC represents the limit of possible loss on this hypothesis, the actual adiabatic will probably lie somewhat below AC, but can never be isentropic, since there must always be a continuous increase of entropy so long as any supersaturation persists.

According to the usual theory of supersaturation, based on the James Thomson isothermal, the SS limit would be reached at the point H, Fig. 17, Chapter VIII, when  $P$  is a maximum (Maxwell, *Theory of Heat*, 1880, p. 290). This would give a pressure  $P_{ss}$  upwards of 100 times that of saturation  $P_s$  in the case of steam at  $50^\circ\text{C}$ ., but assumes a homogeneous transformation, and takes no account of the action of the coaggregated molecules as discrete centres of condensation according to equation (28). Wilson's experiments show that the effective SS limit occurs at a much lower ratio,  $P_{ss}/P_s = 8$ , at low temperatures, but afford no evidence of the constancy of the limiting ratio. According to Maxwell's view, the ratio  $P_{ss}/P_s$  would fall very rapidly with increase of pressure, reaching the value 8 for steam at about  $P_s = 760$  lbs., and diminishing to unity at the critical point. It is theoretically possible that the Wilson ratio, corresponding to a reduction of the mean molecular distance to half the saturation value, might hold throughout the practical range of pressures, but it appears more likely that

there is a continuous diminution in the ratio with fall of surface tension  $\gamma$ . H. M. Martin ("New Theory of the Steam Turbine," reprinted from *Engineering*, Vol. 106, 1918), taking the effective radius of the coaggregation nucleus as remaining constant and equal to  $5 \times 10^{-8}$  cm., and allowing for the variation of  $\gamma$  with temperature, finds values of the pressure-ratio from equation (28) varying from 11 at  $0^\circ$  to 4.8 at  $100^\circ$  C. The curve thus obtained for the SS limit is practically coincident with that shown in Fig. 28 from  $50^\circ$  to  $80^\circ$  C., and gives very similar results when applied to the calculation of the effects of supersaturation at low pressures, where they are most important. There is some indirect experimental evidence, detailed in Chapter XVI, tending to show that the practical SS limit in turbines may be as high as the line of constant wetness QQ in Fig. 28. If this were the case, it would afford a very simple and practical method of calculation, but the actual position of the line remains uncertain at high pressures, though there is every reason to believe that it cannot be lower than the line SS representing the constant ratio 8, which may be safely assumed as representing the maximum limit of loss due to supersaturation. For this purpose we may accept the Wilson ratio provisionally, though it must be admitted that further experiments are desirable.

### 107. Reduction of Efficiency by Supersaturation.

In the case previously considered, it was assumed, in order to simplify the calculation, that the rapidly expanding steam, on reaching the supersaturation limit, was instantaneously transformed into wet saturated steam in the equilibrium state, and remained in this state for the remainder of the expansion. This method gives a *lower limit* for the loss due to initial supersaturation. It is obvious, however, that some degree of supersaturation must persist throughout the whole of the expansion, since the transformation cannot be instantaneous. It is, therefore, desirable to make an estimate of the corresponding upper limit of loss, obtained by assuming the supersaturation line SS.

For this purpose the supersaturation limit may be defined as the limit of the state of *dry* supersaturated steam in rapid expansion which is reached when the pressure is eight times the normal saturation pressure corresponding to the actual temperature of the steam. With this definition it is easy to calculate the properties of steam at the supersaturation limit from the equation for dry steam employed in this work, as shown in the following Table III.

In order to find the limiting form of the *adiabatic* in very rapid expansion it is necessary to make some additional assumption. The simplest and most probable assumption appears to be that the vapour itself remains at the temperature corresponding to the supersaturation limit, so that fresh nuclei are continually being formed throughout the expansion; but that the liquid particles rise very rapidly up to the normal saturation temperature, and are subsequently maintained in the neighbourhood of this temperature by evaporation as expansion continues. The state of the mixture thus defined is easy to calculate, and affords a probable limit to the effect of supersaturation.

If  $H_{ss}$ ,  $V_{ss}$  denote the total heat and volume of the dry vapour at the supersaturation limit as shown in the table, and if  $H_q$ ,  $V_q$  are those of the wet mixture at any stage at the same pressure, we have the simple relation

$$\circ (H_{ss} - H_q)/(H_{ss} - h_s) = (V_{ss} - V_q)/(V_{ss} - v_s), \dots\dots(24)$$

where  $h_s$ ,  $v_s$  are the total heat and volume of the liquid at the normal saturation temperature corresponding to the pressure.

If there is no friction or external heat-loss, we have the simple condition  $dH = aVdP$  defining the adiabatic, but the entropy no longer remains constant, and cannot be calculated by simply adding the entropy of the liquid to that of the vapour, as in the case of wet saturated steam, because the liquid and vapour are at different temperatures and not in equilibrium. The simplest method of finding the adiabatic under these conditions is a step by step process of integration of the fundamental relation. If single and double dashes denote the initial and final states in each step, the drop of  $H$  is readily found with considerable accuracy from the formula

$$\frac{(H' - H'')}{\circ} \frac{(aP'V' - aP''V'')}{\circ} = (\log P' - \log P'')/(\log P'V' - \log P''V''). \dots(25)$$

By assuming an approximate value of  $H''$  from the relation  $dH = aVdp$ , a suitable value of  $V''$  is obtained from the relation between  $H_q$  and  $V_q$ . The formula (25) then gives a very accurate value of  $H' - H''$ , provided only that the pressure range in each step is reasonably small, say not exceeding a ratio 1 to 2.

The values of  $H$  obtained in this way for a particular adiabatic, starting with dry saturated steam at 165 lbs., are shown in the table under the heading "Theor." for comparison with the corresponding values of  $H$  on the usual adiabatic for saturated steam shown in the next column, headed "Sat." Down to a pressure of

56 lbs. the steam is dry, and the values of  $H$  are found from the formula for dry steam. The steam reaches the supersaturation limit at a pressure between 56 and 48 lbs., and the succeeding values are calculated in successive steps. The last column gives the differences between the two adiabatics, and shows that the loss due to supersaturation may become considerable when the expansion is very rapid; but it appears probable that the values given in the table afford a fair estimate of the *limit* of possible loss in the absence of friction. Similar losses must necessarily occur in turbines, but the losses from supersaturation will be reduced when the expansion is less rapid, in proportion as more time is allowed for the approach to the equilibrium state.

Table III.

Properties of Steam at the Supersaturation Limit (F.P.C.).

P	$\frac{p}{p_s}$	$H_{ss}$	$\Phi_{ss}$	$V_{ss}$	$h_s$	$v_s$	Adiabatic from 165 lbs. (dry sat.)			
							Emp.	Theor.	Sat.	Diff.
200	115.59	616.87	1.4299	1.7271	197.80	0.0184				
160	108.87	618.73	1.4553	2.1823	186.63	0.0182	666.10	666.10	666.09	0.01
120	100.58	620.08	1.4863	2.9305	173.53	0.0179	653.08	653.08	652.90	0.18
100	95.55	620.50	1.5052	3.523	165.72	0.0177	645.26	645.26	644.72	0.54
80	89.58	620.68	1.5278	4.407	156.62	0.0175	636.14	636.14	635.01	1.13
64	83.84	620.46	1.5496	5.497	147.97	0.0174	627.47	627.47	625.56	1.91
56	80.49	620.22	1.5627	6.271	143.00	0.0173	622.48	622.48	620.00	2.48
48	76.72	619.80	1.5772	7.295	137.43	0.0172	616.99	616.91	613.70	3.21
40	72.38	619.20	1.5943	8.718	131.08	0.0171	610.51	610.43	606.45	3.98
32	67.23	618.28	1.6148	10.829	123.63	0.0170	602.73	602.64	597.72	4.92
24	60.83	616.86	1.6411	14.302	114.49	0.0169	592.93	592.84	586.85	5.99
16	52.27	614.54	1.6771	21.122	102.43	0.0167	579.54	579.46	572.09	7.37
12	46.49	612.73	1.7022	27.822	94.41	0.0166	570.35	570.27	562.05	8.22
8	38.73	610.08	1.7375	40.98	83.76	0.0165	557.78	557.72	548.37	9.35
5.6	32.25	607.65	1.7683	57.57	74.95	0.0164	547.10	547.07	536.83	10.24
4	26.41	605.37	1.7974	79.31	67.11	0.0163	537.34	537.33	526.37	10.96
2.4	17.99	601.87	1.8410	128.89	55.94	0.0162	523.07	523.09	511.11	11.98
1.6	11.69	599.16	1.8756	189.55	47.66	0.0162	512.22	512.24	499.55	12.69
1.0	4.74	595.79	1.9168	295.71	38.64	0.0161	500.17	500.17	486.68	13.49
0.8	1.59	594.67	1.9357	366.51	34.55	0.0161	494.56	494.56	480.80	13.76

It is comparatively easy to calculate any desired adiabatic for supersaturated steam by the aid of the above table, using the step by step method. But since the theoretical values are somewhat uncertain, it is probably sufficient for practical purposes to estimate the loss below the supersaturation limit by an empirical formula of the type,  $H - B = kP^m$ , with  $m = 1/11$ , and  $B = 228$ , which fits



the adiabatic within a tenth of a caloric as shown by the column headed "Emp." in the above table. The dry part of the adiabatic follows the usual formula for dry steam, with  $m = 8/18$ , and  $B = .64$ . A very fair approximation to the loss of heat-drop in the later stages may be obtained by taking 7.77 per cent. of the heat-drop for saturated steam. The loss at the supersaturation limit is about 5 per cent. of the heat-drop to that point, but tends to a nearly constant *percentage* (7.5 to 8) at low pressures.

The following example illustrates the method of calculation, which is instructive, because it may be applied to calculate any curve of this type, if relations between  $H$  and  $V$ , and  $dH$  and  $VdP$ , are given.

*Example.* Find the adiabatic heat-drop from 8 to 5.6 lbs., taking the initial value  $H' = 557.72$ , (1) for saturated steam at the normal saturation temperature, (2) for supersaturated steam if the temperature of the vapour is at the supersaturation limit, and that of the liquid at the normal saturation point.

To find the initial volume  $V'$  in case (1) we have the usual relation

$$(H_s - H')/(H_s - h_s) = (V_s - V')/(V_s - v_s),$$

which gives  $V' = 40.85$ . In case (2) we have the same relation with  $H_{ss}$ , and  $V_{ss}$  for  $H_s$  and  $V_s$ , and the value of  $V'$  comes out 36.85. A first approximation to the heat-drop  $H' - H''$ , in either case, is obtained from the relation  $dH = aVdP$  by writing it in the form  $ap'V' (dp/p)$ —since  $pV$  changes slowly—and substituting  $p' - p''$  for  $dp$ , and  $(p' + p'')/2$  for  $p$ . This gives for  $H' - H''$  in case (1) 11.86, and in case (2) 10.70, which are in the ratio of the volumes. The resulting values of  $H''$  are 545.86, and 547.02. The corresponding values of  $V''$  are (1) 56.16, and (2) 51.02.

To obtain more accurate values of  $H' - H''$  we may then apply the integrated formula (25). In case (1) we find  $H' - H'' = 11.762$  as a second approximation, which is slightly greater than the difference 11.54, shown in the table for saturated steam between 8 and 5.6 lbs., because the initial state is  $H' = 557.72$  in place of 548.87. In case (2) we find the following values:

$$\begin{array}{lll} ap'V' = 80.82, \log ap'V' = 1.481729, \log p' = 0.90809 \\ ap''V'' = 29.39, \log ap''V'' = 1.468200, \log p'' = 0.74819 \\ \text{Diff.} & 0.98 & 0.013529 \quad 0.15490. \end{array}$$

Whence  $H' - H'' = 0.98 \times 0.15490/0.013529 = 10.650$ , as in the table.

It would appear at first sight as though this were a very inferior

method of approximation, because the result seems to depend on the small difference 0.98 between  $ap'V'$  and  $ap''V''$ , suggesting an order of accuracy of 1 per cent. only. But in reality this small difference is concerned only with a small correction. Thus, if we had taken the rough values  $ap'V' = 30.3$ , and  $ap''V'' = 29.4$ , giving the difference 0.9, we should have found  $H' - H'' = 10.645$ . It is essential however to take the correct values of the *corresponding* logarithms to five significant figures in the *difference*, since the required correction depends on the difference of  $x/\log_e(1+x)$  from unity when  $x$  is small. If  $ap''V'' = ap'V' = 30.32$ , the value of the integral is only changed to  $ap'V' \log_e(p'/p'') = 10.818$ , in place of 10.650.

If we apply the same method of calculation to the expansion from 100 lbs. (dry sat.) to 1 lb., in the case of the nozzle previously illustrated in Table I, we find the adiabatic heat-drop at the supersaturation limit to be only 150.92, as compared with 162.93 at the saturation limit, a reduction of 7.37 per cent., which may be regarded as the limit of probable loss due to supersaturation. The other limit already calculated on the supposition that the steam was transformed into the saturation state as soon as condensation started, gave 161.08 for the heat-drop, showing a much smaller reduction, because it was assumed that there was no further loss when once condensation had started. The loss of heat-drop due to supersaturation after passing the throat, does not affect the mass-discharge, but may materially reduce the efficiency in turbines in which large expansion-ratios are employed for each nozzle.

Since no distinction has hitherto been possible between the effects of friction and supersaturation, all estimates of friction previously made will include any effects of supersaturation. When the expansion is so rapid as it is in a nozzle with a large expansion-ratio, it is very likely that the state of the steam will remain very near the SS limit throughout the latter part of the expansion. Thus if we take 15 per cent. as the whole loss for a nozzle of this size, about half will be due to friction and the other half to supersaturation. The supersaturation loss would be independent of the size of the nozzle, but the friction loss would be less for larger sizes. The final velocity remains the same for the same heat-drop, and is unaffected by the hypothetical subdivision of the loss as between friction and supersaturation. But if we suppose the final state to be approximately at the SS limit in spite of friction, there will be an appreciable diminution in the final volume as previously cal-

culated. With the same heat-drop, namely 185.1, at the SS limit, the volume comes out 259.1 in place of 288.8 at the saturation limit, and the value of  $X/M$  is reduced from 11.69 to 10.69. Further, if half the effect previously attributed to friction is really due to supersaturation, the numerical value of the coefficient previously suggested for friction should also be reduced to one half. But the experimental data are difficult to interpret, and do not justify any certain conclusion.

**108. Stodola's Experiments on Nozzle Friction.** Stodola (*Steam Turbines*, p. 52) measured the pressure at various points in a conical nozzle, and deduced the probable effects of friction by comparing the results with a theoretical calculation of the pressures on the assumption that the steam was in the equilibrium state of saturation throughout the discharge. It may be of interest to recalculate these observations on the assumption that the steam was in reality supersaturated. The nozzle employed had a diverging cone about 16 cms. long, with an angle of  $8^{\circ} 49'$ , and a throat diameter of 1.25 cm. The pressures were measured by connecting gauges to four small holes through the sides of the cone, and also by a central exploring tube, 5 mm. in external diameter, adjustable in position by means of a screw. The curve marked  $X_0$  in the annexed Fig. 24 shows the effective cross-section of the conical part of the nozzle, allowing for the exploring tube, in relation to distance  $x$  measured along the nozzle in cms. from the throat. The curve is continued in the figure beyond the end of the actual nozzle to lower pressures, assuming the cone angle to remain the same. The curve marked  $P_0$  shows the pressures in kg./sq. cm. calculated for frictionless expansion at the SS limit. The observed pressures, indicated by the dots, are necessarily higher than the calculated pressures owing to friction. It was difficult to obtain steady readings of pressure above 1 kg./cm.<sup>2</sup> owing to the excessively rapid drop of pressure and total heat in the first 5 cms. of the cone. The curve  $DH_0$  indicates the drop of total heat in the same cone at the SS limit. In order to get uniform *acceleration* of the steam, which would probably permit steady readings, it would be necessary that the curve of heat-drop  $DH$  should be a straight line, such as  $DH_0$  (dotted), when plotted against  $x$ . The curve marked  $X_u$  represents the required cross-section of the nozzle for uniform heat-drop per cm.: the curve  $P_u$  shows the corresponding pressures. In this case the section would no longer be a simple cone, but would be nearly

uniform for some distance beyond the throat. This form of nozzle might be suitable for experimental purposes, but would be difficult to make as compared with the simple cone, and would involve increasing the length of the nozzle for the same expansion from 16 to over 20 cms., with an increased angle of divergence at the end. The increase of angle could be avoided by a little extra length, but for purely practical purposes the simple cone might be best.

*Value of the Discharge.* The observed value of the discharge during the tests is given as  $M = 0.153$  kg./sec., corresponding to an initial state,  $P_0 = 10.48$  kg./cm.<sup>2</sup>,  $t_0 = 198^\circ$  C., from which we obtain the following values,  $H_0 = 676.0$  cal. C.,  $\Phi_0 = 1.5964$ ,

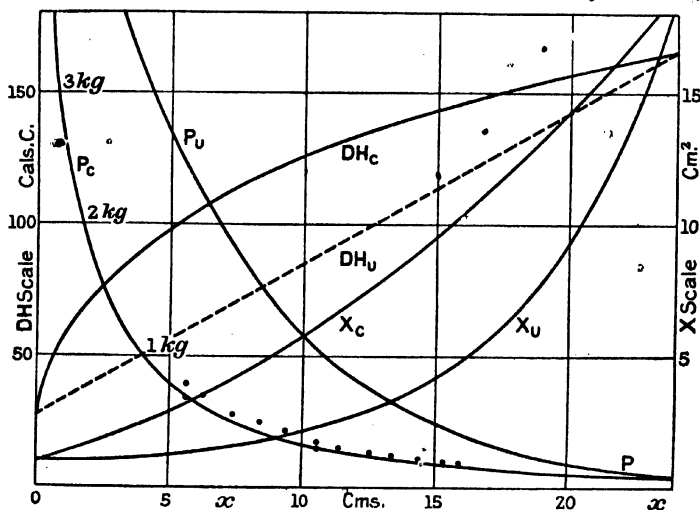


Fig. 24. Pressures observed by Stodola in a Conical Nozzle.

$G_0 = 76.1$ ,  $V_0 = 0.2000$  cb. m./kg., required for calculating the isentropic heat-drop to any lower pressure.

The effective cross-section of the throat, allowing for the exploring tube, is  $1.030$  cm.<sup>2</sup>. The discharge calculated for the initial state of dry saturated steam at  $10.48$  kg./cm.<sup>2</sup>, with  $V_s = 0.1912$ ,  $t_s = 181.0^\circ$  C., by the usual formula,  $M/X_t = 0.0199 (P_0/V_s)^{1/2}$ , assuming the steam to be saturated in the throat, comes out  $M = 0.1516$  kg./sec. Allowing for the fact that the initial steam was superheated  $17^\circ$  C., but still supposing the steam to be saturated before reaching the throat, the calculation of the discharge is more troublesome, since it is necessary to find by trial the pressure at

which  $X/M$  is a minimum. The result found in this way is  $M = 0.1584$  kg./sec., which shows a slight increase due to the superheat, and agrees very closely with the observed discharge, namely  $0.156$  kg./sec., but leaves very little margin to allow for any reduction due to friction.

If on the other hand we assume that the steam is still dry and supersaturated on reaching the throat, and calculate the discharge in both cases by the same formula with the coefficient  $0.0209$  in place of  $0.0199$ , we find

For steam initially saturated at  $181^\circ \text{C.}$ ,  $M = 0.1592$  kg./sec.

For steam initially superheated at  $198^\circ \text{C.}$ ,  $M = 0.1559$  kg./sec.

showing a diminution of the discharge with superheat, which agrees with the interpretation of Mellanby's experiments given in section 105.

In this case it is necessary to suppose that the effect of throat friction is to reduce the discharge from  $0.1559$  to  $0.153$  kg./sec. According to the formula  $1/P_0 D$  (F.P.C.) suggested in section 104, for the fractional reduction due to throat friction, with  $P_0 = 149$  lbs./in.<sup>2</sup>, and  $D = 0.5$  in., the reduction should be 1.8 per cent.; but the presence of the exploring tube increases the frictional surface in the proportion of  $7/5$ , giving a probable reduction of 1.8 per cent., which happens to agree exactly with the reduction from  $0.1559$  to  $0.153$  kg./sec.

*Estimate of Frictional Loss.* Stodola estimated the loss by drawing a curve similar to  $P_0$  in the previous figure, giving the pressure distribution along the nozzle for frictionless expansion at the saturation limit; and by adding two similar curves for a reduction of 10 per cent., and 20 per cent., respectively, in the heat-drop at each pressure. For a given value of the discharge, such as  $M = 0.153$ , it is easy to calculate the values of  $X$  and  $x$  corresponding to any assumed value of  $P$  with 0, 10 per cent., and 20 per cent. loss, respectively, in the following manner. Find  $DH_0$  for the assumed  $P$ , deduct 10 per cent. and 20 per cent., and find the corresponding values of  $U$  and  $V$ . Deduce  $X$  from the formula  $X = 10,000MV/U$  (K.M.C.), and find the value of  $x$  allowing for the exploring tube.

For instance, at

$P = 0.844$  kg. (12 lbs.),  $H_0 = 637.02$ ,  $V_0 = 2.021$  (K.M.C.).

Isentropic  $DH_0 = 103.89$ ,  $U = 932.6$ ,  $V = 1.779$ ,  $X = 2.918$ ,  $x = 5.01$  cms.

Loss 10%  $DH = 93.50$ ,  $U = 884.8$ ,  $V = 1.818$ ,  $X = 3.143$ ,  $x = 5.46$  „

Loss 20%  $DH = 83.11$ ,  $U = 834.2$ ,  $V = 1.857$ ,  $X = 3.405$ ,  $x = 5.98$  „

By calculating a few points in this way, the required curves are readily drawn. The observed pressures for  $M = 0.158$ , plotted as dots on the same scale, show the loss at each point of the nozzle by their position in relation to the calculated curves. Stodola's curves show a loss of about 10 per cent. at a pressure of 0.8 kg., increasing to about 20 per cent. at 0.2 kg., and suggesting even larger losses at lower pressures. But these losses seemed rather large to attribute simply to friction, and he concluded from other experiments that the total loss for the nozzle investigated did not exceed 15 per cent.

The above method of estimating the loss is very simple and direct, but it gives a somewhat restricted scale at low pressures, where the loss is most important, and it does not exhibit the loss itself in the form of a curve on a uniform scale. It also proves inconvenient for showing the effects of supersaturation in contrast with those obtained on the usual assumption that the steam is in the equilibrium state of saturation throughout the expansion. For these reasons the same observations are reduced by a different method in the annexed figure, the actual loss calculated for each point observed being plotted against the isentropic heat-drop at the same pressure.

**109. Curve representing Loss of Heat-Drop.** The abscissa in the annexed Fig. 25 is the isentropic heat-drop  $DH_\phi$  in calories C. at any pressure, representing the limit of possible performance; the ordinate is the loss of heat-drop at the same pressure, plotted on a five times larger scale. The curve ACD represents the defect of heat-drop along the dry adiabatic starting with the initial state  $P = 10.48$ ,  $t = 198^\circ$  (K.M.C.). A represents the point at which the steam reaches the saturation limit, with  $DH_\phi = 18$  nearly. The point B corresponds with the throat of the nozzle. The supersaturation limit is reached at the point C, where  $DH = 56.4$ , and  $DH_\phi = 59.4$ , with a loss of 8 cal., or 5 per cent. The curve CSS is the adiabatic at the supersaturation limit, which is not isentropic, the entropy increasing from 1.5964 before condensation starts, to 1.6048 at C after condensation starts, and to 1.6405 at a pressure of 1 lb. near the end of the curve CSS. The curve CS, which is nearly a straight line, represents the assumption that the steam remains at the saturation limit, without further increase of entropy, after passing the point C. The value of the entropy at any point when the steam is not in a state of equilibrium is estimated from the formula

$\Phi = (H + G)/T$ , by supposing it transformed to the equilibrium state at constant pressure. The point at which the SS limit is reached in the absence of friction may be found from the table SS by taking the pressure (about 89 lbs. in this case) at which  $\Phi_{ss}$  is equal to the initial value 1.5934.

The small circles in the figure represent the observations of Stodola as reduced on the assumption that the steam is in the state of saturation. The whole loss in this case is attributable to friction

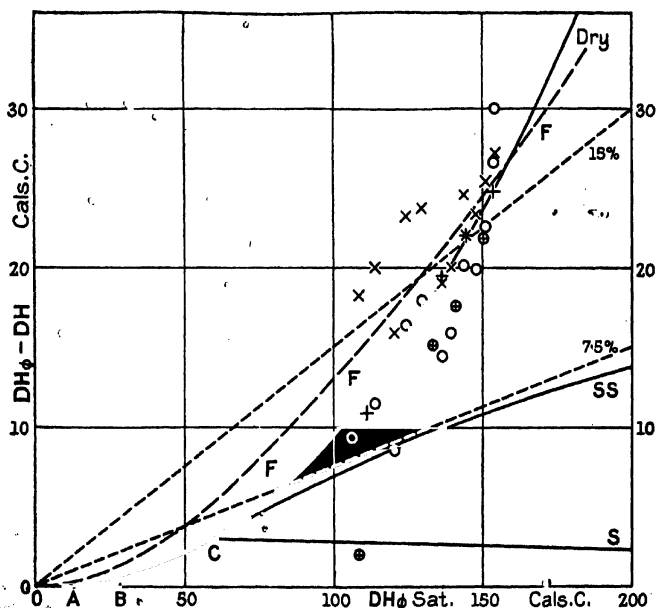


Fig. 25. Loss of Heat-Drop due to Supersaturation.

alone. The crosses not enclosed in circles represent the reduction of the same observations on the assumption that the steam is at the SS limit, represented by the curve CSS. The loss due to friction in this case is measured by the height of the crosses above the curve CSS, the remainder of the loss, below the curve, being attributable to supersaturation.

Taking first the circles, representing the usual hypothesis of saturation, it will be seen that they lie roughly on a curve rising very steeply at low pressures, and reaching a maximum loss of

80 cal., or 20 per cent. of the isentropic heat-drop at the end of the nozzle, where  $P = 0.20$  kg./cm.<sup>2</sup>.

*Method of Calculation.* The method of calculation for the separate observations is much the same as that previously given for the curves, but is performed in the reverse order. In the previous case,  $P$  and  $DH$  are assumed and it is required to find  $X$  and  $x$ . In the case of the observations,  $P$  and  $x$  are given, and  $DH$  is required. As an example of the method we may take the first observation,  $P = 0.742$ , at the point  $x = 5.67$  in the side of the nozzle.

$x = 5.67$  gives  $X = 3.248$ , whence if  $M = 0.153$ , we have  $U/V = 471.0$ .

$P = 0.742$  gives  $DH_{\phi} = 108.88$ ,  $H_s = 635.59$ ,  $H_s - st = 544.9$ ,  $V_s = 2.280$ .

Taking  $DH = 100$  gives  $U = 915.1$ ,  $H_s - H = 59.59$ ,  $V = 2.080$ ,  $U/V = 450.7$ .

Taking  $DH = 107$  gives  $U = 946.6$ ,  $H_s - H = 66.59$ ,  $V = 2.002$ ,  $U/V = 472.8$ .

By interpolation at  $U/V = 471.0$ , we obtain  $DH = 106.4$ , whence the loss is 2.0.

The pressure at the same point,  $x = 5.67$ , observed with the central exploring tube, was 0.797, giving  $DH_{\phi} = 106.2$ ,  $DH = 96.6$ , loss = 9.6 cal. C., suggesting that there was a real difference of pressure between the centre and side of the jet at this point, owing to the too rapid increase of section of the cone. The mean loss for the whole section would probably be intermediate between the two, about 6 cal. at  $DH_{\phi} = 107$ . The four observations taken at the side of the nozzle are marked with crosses (+) enclosed in the circles. The remaining three of these are seen to agree as closely as could be desired with the plain circles representing the observations with the central exploring tube.

It is evident that the curve of frictional loss deduced from these observations, on the assumption that the steam is saturated, is of a highly improbable character. The curve is much too steep, and tends to cut the axis, giving zero or negative loss at pressures above 1 atmosphere; while it gives losses which are too large to attribute purely to friction at low pressures. These peculiarities cannot be attributed entirely to errors of observation, in spite of the great difficulties of the experiments. They appear to be chiefly due to the error of the assumption that the steam is in the equilibrium state of saturation; but there may also be some small systematic errors



in the pressure measurements, which require consideration when dealing with steam at such extremely high velocities.

*Correction of the Pressures.* When steam or other fluid is flowing parallel to a surface with high velocity, the pressure near the surface will be raised by the frictional retardation of the stream. The pressure in a small hole at right angles to the surface, being the same as the pressure at the surface, will be higher than the pressure in the main body of the stream. Moreover, an exploring tube with its length parallel to the stream, and provided with a small opening at right angles to its surface, will have all its indications raised by friction in a similar manner, so that the effect in question cannot easily be detected or measured experimentally. There is no certain method of calculating the effect in the case of turbulent flow, but the rise of pressure at the surface will evidently be proportional to the velocity-head, which is  $U^2/2gV$  in gravitational units, and is commonly measured with a Pitot tube. At ordinary velocities, such as are familiar in aeronautical tests, the velocity-head is insignificant as compared with the absolute pressure to be measured and the error is negligible; but in a steam-nozzle, where the velocity-head at low pressures may be four or five times the absolute pressure of the medium, the correction may evidently become very important, even if it is only a small fraction of the velocity-head.

Since  $DH$  is proportional to  $U^2$ , and  $X$  is proportional to  $V/U$ , the velocity-head, and the required pressure-correction, may be taken as proportional to  $DH/V$ , or to  $U/X$ . Although the absolute magnitude of the correction is unknown, the relative values are fairly certain, and it is easy to try the effect of assuming different absolute values. Taking the correction as 0.018 at 0.20 kg./cm.<sup>2</sup>, near the end of the expansion, it would amount to 0.042 on the first observation at 0.742 kg. Repeating the calculation with the corrected pressures, the loss at the lowest pressure is reduced by more than a half, but the loss at  $P = 0.742$  becomes negative, and the loss curve tends to cut the axis at a higher point near 110. This correction does not help to explain the observations satisfactorily on the assumption that the steam is saturated. The assumption of the state represented by the curve CS makes little difference. We conclude that the state must be something nearly approaching the curve CSS, representing the supersaturation limit.

**110. Effect of Supersaturation.** If the supersaturation limit is assumed to represent the probable state of the steam, the

method of calculation is exactly the same as for saturated steam, except that the expansion curve follows the dry adiabatic as far as the point C, and that the relation employed in deducing  $V$  from  $H$  is that appropriate to the SS limit. If the observed values of the pressure are employed without correction, the observations, when plotted, give a curve which does not show any tendency to cut the axis, as in the previous case, but gives rather high values at low pressures, reaching 89.5 cal. or 25 per cent. at 0.20 kg., of which about 7 per cent. would be attributable to supersaturation and 18 per cent. to friction. The pressures were accordingly corrected by deducting 2 per cent. of the velocity-head at each point. The results thus obtained are shown by the plain crosses, (  $\times$  ) for the observations with the central exploring tube, and (  $+$  ) for those taken through the side of the nozzle. The loss at 0.20 kg. is then about 17 per cent. of which 10 per cent. is debited to friction. If the circles representing the reduction of the observations on the saturation hypothesis are disregarded, it will be seen that the observations fit fairly with the dotted curve FF, in drawing which the frictional loss is represented by the empirical term  $0.006 DH_0^2$  added to the curve ACSS representing the supersaturation loss. This is the simplest type of formula by which the observations can be represented with any degree of probability, but the observations are not sufficiently consistent, and do not extend far enough to exclude a variety of other assumptions. It is quite possible that the pressure-correction should be increased to 3 per cent. of the velocity-head, in which case the loss attributable to friction would be further reduced to about 6 per cent. at 0.2 kg., but the curve would still be of a probable type. The hypothesis of supersaturation evidently affords a possible explanation of the observations, besides being intrinsically probable on other grounds. It is also required to explain the great improvement effected by a moderate degree of superheat, which follows naturally if the supersaturation loss is a large fraction of the whole, but cannot be explained satisfactorily on theoretical grounds if the steam is saturated.

**III. Effect of Superheat.** In order to make an estimate of the probable effect of superheat in improving the efficiency of a nozzle, we may consider the reduction of supersaturation separately from that of friction, to the reduction of which alone the improvement has generally been attributed. Since the motion is turbulent, the effect of superheat on the friction cannot be predicted with

any degree of certainty, but it is possible to calculate the reduction of the supersaturation loss by assuming the expansion to proceed at the SS limit in the absence of friction, and the result so obtained will apply with close approximation in the presence of friction on the well-known principle of the independence of small corrections.

To facilitate the calculation we require in the first place a simple rule for deducing the adiabatic heat-drop in expansion at the SS limit. It has already been shown that, for a large range of expansion, when the initial state is dry saturated, the loss due to supersaturation at the SS limit approximates very closely at low pressures to a constant percentage, 7.78 per cent., of the adiabatic heat-drop for saturated steam under the same conditions. When the initial state is one of superheat, the two expansion curves coincide so long as the steam is superheated, but the percentage reduction remains very nearly the same for that part of the expansion which is below the saturation limit. The rule for finding the adiabatic heat-drop for supersaturated steam at the SS limit in the case of initial superheat is consequently as follows:

**Rule.** Find the adiabatic heat-drop  $DH_\phi$  for saturated steam under the same conditions, and deduct 7/90, or 7.78 per cent., of that part of  $DH_\phi$  which is below the saturation limit.

As an example of this rule we may take the case of the nozzle last considered, in which the initial state was  $p = 10.48$ ,  $t = 198^\circ$  (K.M.C.), giving  $\Phi = 1.5964$ ,  $H = 676.0$ ,  $t_s = 181.0^\circ\text{C.}$ , superheat  $17^\circ\text{C.}$

The adiabatic heat-drop for saturated steam from this initial state to a final pressure 2.4 lbs., or 0.16874 kg., is found by the usual rule to be  $DH_\phi = 155.86$  cal. C. With  $\Phi = 1.5964$ ,  $H_s = 668.55$  from Table II, App. III, the steam reaches the saturation limit after a drop of 12.45 cal., leaving 143.41 as the part of  $DH_\phi$  below the saturation limit. To find the loss of heat-drop due to supersaturation we take 7/90 of 143.41, giving 11.14 cal. Subtracting this from  $DH_\phi$ , we obtain  $DH_{ss} = 144.62$  as the adiabatic heat-drop at the SS limit. This result is the same to the last figure as that obtained by the somewhat laborious process of integrating  $aVdP$  with the aid of Table SS.

The method of calculation, and the reduction of the SS loss by superheat, may be illustrated graphically by supposing the curve ACSS in the last figure shifted to the right as the superheat is increased. In the present case the required correction may be read

directly from the curve, which is drawn for  $17^\circ$  superheat, by taking the ordinate at 155.86, namely 11.2 cal.

To find the effect of a moderate degree of superheat in reducing the SS loss for this particular nozzle, it will be sufficient to calculate  $DH_\Phi$  and  $DH_{ss}$  for two cases, (1) initial state dry saturated, and (2) with initial superheat such that the steam is just saturated on reaching the throat. The initial states for the same pressure,  $P = 10.48$  (K.M.C.), are

(1)  $t = 181.01^\circ \text{C.}$ ,  $\Phi = 1.5770$ ,  $H = 666.41$ ,  $V = 0.1910$ ,  
 $G = 49.74$  (K.M.C.).

(2)  $t = 220.58^\circ \text{C.}$ ,  $\Phi = 1.6244$ ,  $H = 688.80$ ,  $V = 0.2121$ ,  
 $G = 118.08$  (K.M.C.).

In finding (2), to make the steam just saturated on reaching the throat, the value of  $P_t$  is taken as  $0.5457P_0 = 5.72$ , giving  $\Phi_t = 1.6244$ ,  $t_t = 156.18^\circ \text{C.}$  in the throat. The values of  $t_0$ ,  $H_0$ ,  $V_0$ , and  $G_0$ , are found by interpolation with this value of  $\Phi$  in Tables VI, IV, V, and VII.

An approximate solution may be obtained by taking the same final pressure, 2.4 lbs., or 0.16874 kg., in each case, which gives the results

(1)  $DH_\Phi = 152.7$ ,  $DH_{ss} = 140.8$ ,  $U = 1086$ ,  $V = 6.921$ ,  
 $U/V = 156.9$  (K.M.C.).

(2)  $DH_\Phi = 159.5$ ,  $DH_{ss} = 149.4$ ,  $U = 1118$ ,  $V = 7.124$ ,  
 $U/V = 157.0$  (K.M.C.),

showing an apparent improvement in  $DH_{ss}$  amounting to 8.6 cal. C. But since the values of  $U/V$  do not fit with those of  $M/X$  for the final section of the nozzle, it is necessary to repeat the calculation at a second pressure in order to allow for the effect of superheat in altering the discharge  $M$  and the final pressure which the nozzle is capable of utilising efficiently.

Repeating the calculation for  $P = 2.2$  lbs. or 0.1547 kg., we obtain

(1)  $DH_\Phi = 155.2$ ,  $DH_{ss} = 148.1$ ,  $U = 1095$ ,  $V = 7.494$ ,  
 $U/V = 146.1$  (K.M.C.).

(2)  $DH_\Phi = 162.1$ ,  $DH_{ss} = 151.8$ ,  $U = 1127$ ,  $V = 7.712$ ,  
 $U/V = 146.1$  (K.M.C.).

It will be seen that superheat does not appreciably affect the values of  $U/V$ , which are nearly the same in (1) and (2) at the same final pressure. But it reduces the discharge, and alters the pressure

at the final section of the nozzle,  $X = 10.47$  cm.<sup>2</sup>. Taking the throat section as 1.08 cm.<sup>2</sup>, we have (1)  $M = 0.1594$  kg./sec., (2)  $M = 0.1518$ , so that the final values of  $U/V$  in either case must be (1)  $U/V = 152.2$ , (2)  $U/V = 144.5$  (K.M.C.). By interpolation with these values of  $U/V$  we obtain the final values (1)  $P = 0.1627$  kg.,  $DH_{ss} = 141.8$ , (2)  $P = 0.1545$  kg.,  $DH_{ss} = 152.2$  (K.M.C.) showing an improvement in heat-drop of 10.4 cal. for 89.5° C. superheat, or 1 per cent. for each 5.4° C. of superheat, which agrees fairly with observation.

If we make a similar calculation on the hypothesis that the steam is in the state of saturation, with the corresponding values of  $M$  and  $U/V$ , namely, (1)  $M = 0.1518$ ,  $U/V = 145.0$ , (2)  $M = 0.1518$ ,  $U/V = 144.5$  (K.M.C.), we obtain by interpolation the final values of  $P$  and  $DH_{\phi}$ , for saturation, (1)  $P = 0.1584$  kg.,  $DH_{\phi} = 154.5$ , (2)  $P = 0.1600$  kg.,  $DH_{\phi} = 161.1$  (K.M.C.), showing an improvement of heat-drop of only 6.6 cal., or 1 per cent. for each 9.8° C. of superheat, which is a much slower rate of improvement than is commonly obtained in practice. It will be seen that there is no improvement in the final pressure with superheat, but rather the reverse, if the calculation is made on the saturation hypothesis, and that part of the improvement of heat-drop in the case of supersaturation is due to the reduction of the final pressure. It is necessary to take account of this in making the comparison, because the change in the appropriate final pressure will inevitably produce some effect on the performance even if the vacuum is not varied.

The calculation of the effect has been made in the absence of friction, but the presence of friction will tend if anything to increase the advantage gained by the elimination of supersaturation loss. There may be some reduction of friction with superheat, but the amount of frictional loss and its mode of variation are too uncertain to be a profitable subject for calculation.

**112. Discharge through a Series of Throttles.** The case of a series of similar throttles traversed by the same flow  $M$ , is of interest in relation to the theory of "labyrinth" glands and packings in which leakage is reduced by repeated throttling through small apertures. If there are  $N$  throttles, and if the sectional area  $X$  of each is the same, a simple solution is readily obtained on the following assumptions: (1) that the steam is dry, and that  $H$  remains constant, (2) that the drop of pressure at each throttle is small, and (3) that the pressure at the throat of each throttle is equal to the corresponding back-pressure. If the initial steam is dry,

assumption (1) requires that the product  $PV$  shall remain very nearly constant (neglecting  $b$ ) and equal to the initial value  $P_0V_0$ . The flow is defined by the simple relations

$$144M/X = U/V, \text{ where } V = P_0V_0/P, \text{ and } U = 30C(aVdP)^{1/2}.$$

Substituting for  $U$  and  $V$  we obtain immediately

$$\begin{aligned} 2(144M/300X)^2 (P_0V_0/a) &= 2PdP \\ &= d(P^2) = P_0^2 - P_1^2 = (P_0^2 - P_N^2)/N, \therefore (26) \end{aligned}$$

where  $P_N$  is the back-pressure after passing the last throttle.

Transposing and reducing, we find for  $M/X$  in lbs. per sec. per sq. in.,

$$M/X = 0.473 \sqrt{(P_0^2 - P_N^2)/NP_0V_0} \quad (\text{F.P.C. or F.}) \dots (27)$$

The value of the constant for (K.M.C.) units is 0.0313. A formula of a similar type, but deduced by a somewhat different method, was given by Martin, *Engineering*, Jan. 1908, p. 35, *Steam Turbines*, pp. 166-171.

In many cases which occur in practice the number of throttles  $N$  is insufficient in comparison with the pressure range to permit of condition (2) being satisfied to a satisfactory degree of approximation. The discharge in this case will generally be limited by reaching the maximum value when the pressure-ratio for the last throttle exceeds the critical value 0.5457. In this case, the pressure  $P_N''$  in the throat of the last throttle may considerably exceed the final back-pressure, so that the previous solution no longer applies. The discharge through the last throttle is then given by the usual formula

$$\begin{aligned} M/X &= 0.3155 (P'/V')^{1/2} \quad (\text{F.P.C. or F.}), \\ &= 0.0209 (P'/V')^{1/2} \quad (\text{K.M.C.}), \end{aligned}$$

where  $P'$ ,  $V'$ , are the pressure and volume before the last throttle. Substituting  $P_N = 0.5457P'$ , and  $P'V' = P_0V_0$ , in accordance with (1),

$$M/X = 0.578 (P_N/P_0) (P_0/V_0)^{1/2} \quad (\text{F.P.C. or F.}) \dots (28)$$

The value of the constant for (K.M.C.) units is 0.0383.

The pressure ratios for the other throttles can be calculated in succession by the formula of de St Venant and Wantzel. By compounding these ratios, the required value of  $P_N/P_0$  can be tabulated for any number of throttles, as in the following table extending to 50 throttles. It is then easy to calculate the theoretical value of  $M/X$  for any case in which the ratio of the back-pressure to the initial pressure is less than that tabulated for the corresponding

number of throttles, so that the critical value of the pressure ratio will be reached for the last throttle, and the discharge will be independent of the back-pressure for any value lower than  $P_N$ .

Table IV.

Critical ratio of final to initial pressure for  $N$  similar throttles.

$N$	$P_N/P_0$	$N$	$P_N/P_0$	$N$	$P_N/P_0$	$N$	$P_N/P_0$	$N$	$P_N/P_0$
1	5457	11	2280	21	1702	31	1418	41	1242
2	4432	12	2194	22	1666	32	1397	42	1228
3	3854	13	2117	23	1632	33	1377	43	1214
4	3463	14	2048	24	1600	34	1358	44	1201
5	3174	15	1985	25	1570	35	1339	45	1188
6	2949	16	1928	26	1541	36	1321	46	1175
7	2767	17	1876	27	1514	37	1304	47	1163
8	2616	18	1828	28	1488	38	1288	48	1152
9	2487	19	1783	29	1464	39	1272	49	1140
10	2376	20	1741	30	1440	40	1257	50	1129

NOTE. The decimal point is omitted before the first figure in each ratio.

If the ratio of the final to the initial pressure is *greater* than the critical value tabulated for the given number of throttles, the table can still be employed for finding theoretical values of  $M/X$  by interpolation. Thus if the ratio of the back-pressure to the initial pressure is 1 to 2, we have to find two values of  $P_N/P_0$  in this ratio in the table separated by the given number of throttles. Thus the ratio 0.1140 for  $N = 49$ , is just half the ratio 0.2280 for  $N = 11$ , or 38 throttles would suffice to give a reduction of pressure in the ratio 1/2 when the value of  $M/X$  is that obtained by putting 0.1140 for  $P_N/P_0$  in the theoretical formula (28). If there were only 20 throttles, the range  $N = 5$  to 25 gives a ratio  $1570/8174 = 1/2.022$ , and the range  $N = 6$  to 26 gives  $1541/2949 = 1/1.914$ . By interpolation we find 0.1564 as the appropriate value of  $P_N/P_0$  for 20 throttles with a pressure-ratio 1/2. It would evidently be quite near enough for the purpose to take the nearest value 0.1570, in the table, without troubling to do the interpolation. The maximum discharge for 20 throttles is reached with any back-pressure ratio less than 0.1741, corresponding to  $N = 20$  in the table. But an increase of the back-pressure ratio to  $0.1702/0.5457 = 0.312$ , corresponding to the next step of 20 in the table, from  $N = 1$  to 21, reduces the discharge in the ratio  $0.1702/0.1741$ , only, so that no great accuracy of interpolation is ever required. It is less trouble to use the table than to work out the approximate formula, with

the advantage that the results are theoretically more accurate, especially if the number of throttles is small. Martin's formula is more accurate in extreme cases than the approximate formula (27), but it is also more trouble to work. The approximate formula necessarily agrees in the limit with the table when the number of throttles is large and the pressure ratio small, but the errors are surprisingly small for so simple a formula even when the number of throttles is small and the pressure ratio large, as is seen in the following example.

Table V.

Initial pressure 165 lbs. (dry sat.), back-pressure 20.6 lbs.

Number of throttles	4	9	16	25	36	49
Discharge $M/X$ table	1.540	1.107	0.858	0.698	0.588	0.507
„ by approx. formula	1.805	1.203	0.903	0.722	0.602	0.516
„ by Martin's formula	1.464	1.084	0.849	0.694	0.585	0.505

Martin's formula gives results which are always a little too small, but the error is insignificant. The theory appears to be reliable for comparative values, but assumption (3) is somewhat uncertain, since the throat-pressure may be less than the back-pressure. It is most important in practice to make the clearance  $X$  as fine as possible, and to take care to avoid any possibility of a direct blow-through or carry-over of velocity from one throttle to the next.



## CHAPTER XI

### FLOW THROUGH A TURBINE

**113. Impulse and Reaction.** It would be outside the scope of the present work to describe mechanical details of construction and operation of turbines, for which the reader must be referred to other works. It will be necessary, however, to explain the general principles of the flow through a turbine in a few ideal cases, in order to elucidate the application of the thermodynamical formulæ.

If a jet of fluid strikes a moving blade with relative velocity  $U_r'$ , the quotient  $U_r'/g$  may be regarded as expressing in gravitational measure the "impulse" of the jet on the blade, per unit mass of fluid, acting in the direction of  $U_r'$ . If the same jet leaves the blade with relative velocity  $U_r''$ , the quotient  $U_r''/g$  may similarly be regarded as the "reaction" of the jet on the blade, and acts in the direction opposite to  $U_r''$ . The resultant of the impulse and reaction, taken with due regard to sign, will represent correctly in all cases the whole action of the fluid on the blade, but the forces of impulse and reaction can seldom be regarded as possessing a separate physical existence otherwise than as mathematical components of the resultant.

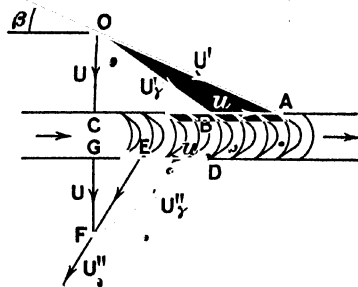
If the blade is moving with a velocity  $u$  in a direction making an angle  $\beta'$  with the impulse, and an angle  $\beta''$  with the reaction, the work  $W$  done by the jet on the blade per unit mass of fluid is obtained by adding the resolved parts of the impulse and reaction in the direction of motion, and multiplying the sum by the velocity  $u$ .

$$W = (U_r' \cos \beta' + U_r'' \cos \beta'') u/g. \dots\dots\dots(1)$$

This simple formula includes all cases, but its application depends on the possibility of specifying the directions and velocities, which cannot be done exactly except in a few ideal cases. The following sections illustrate two such limiting cases representing types of flow which can be approximately realised in practice, and which are most commonly aimed at in the construction of

**114. The Impulse Turbine.** The simple impulse wheel carries a rim of semi-cylindrical blades, shaped somewhat as shown in the annexed Fig. 26, in which the blade rim is seen developed in section. Steam issuing from a nozzle at the side (not shown in the figure) with velocity  $U'$ , represented by  $OA$ , inclined at a small angle  $\beta$  to the plane of the wheel, has a normal component  $OC = U = U' \sin \beta$ , at right angles to the wheel, and a tangential component

Fig. 26.



**Fig. 26.**

$$CA = U' \cos \beta$$

in the direction of rotation. If the blades are revolving with mean velocity  $u$ , represented by BA, the tangential component of the relative velocity  $U_r$  is evidently  $U' \cos \beta - u$ , and is represented by CB. In the ideal case, neglecting friction and compression, the blades are shaped so that the cross-section of the channel between them, estimated at right angles to the flow, is uniform, in which case the steam will flow through without change of pressure or velocity. If the blades are symmetrical, the angle of exit, FDG, will be equal to the angle of entrance, OBC. The tangential component of the reaction due to DF, is the same as that of the impulse due to OB, and the expression\* for the work is evidently

$$W = 2 (U' \cos \beta - u) u/g = 2 (z - 1) u^2/g, \dots\dots\dots(2)$$

where the symbol  $z$  is employed as a convenient abbreviation for the ratio of the tangential component  $U' \cos \beta$  of the steam-velocity to the blade-velocity. The absolute velocity of exit,  $U''$ , represented by EF, has a tangential component,  $EG = U' \cos \beta - 2u$ . The axial component  $U$  of  $U''$  is the same as that of  $U'$ . In the absence of friction, the drop of kinetic energy  $(U'^2 - U''^2)/2g$ , is equal to  $W$ ; but exceeds  $W$  by the work wasted when friction is

present, in which case  $U''$  will be less than  $U'$ . The general expression for  $W$  in terms of the relative velocities still holds, so that the drop of relative velocity can be estimated if the friction is known, or conversely the frictional loss can be estimated from the drop of  $U$ .

**115. The Reaction Turbine.** The most characteristic feature of the reaction turbine, as distinguished from the impulse turbine, is that the moving blades, or vanes, are exactly similar to the fixed blades, or guides, but are oppositely directed. The effect of this is that drop of pressure and increase of velocity occur equally in both fixed and moving blades; whereas there is no drop of pressure or increase of velocity in the moving blades of the impulse turbine in the ideal case.

In an axial flow turbine of the Parsons' type, the axial velocity  $U$  of the steam, represented by the line OC in the annexed Fig. 27, is determined at any stage by the relation  $U = kMV/X$ , where  $X$  is the cross-section of the annular space between the drum or rotor carrying the vanes and the cylinder or casing to which the guides are fixed. The steam is deflected by the guides, and its velocity is increased to  $U'$ , represented by the line OA in the figure, making an angle  $\alpha$  with the axis or  $\beta$  with the tangent, so that  $U' = U \sec \alpha$ , or  $U = U' \sin \beta$ . If the vanes are moving with velocity  $u$ , represented by the line BA, the relative moving velocity  $U''$  with which the steam meets the vanes is represented by the line OB, the tangential component of which is

$$CB = U' \cos \beta - u = U \tan \alpha - u.$$

In a continuous series of similar pairs of vanes and guides, the flow will be symmetrical, and the axial component  $U$  of the velocity will remain constant if provision is made for the gradual expansion of the steam by increasing  $X$ . The relative velocity  $U'$  with which the steam leaves the vanes, will be the same as that with which it left the guides, and the absolute velocity  $U''$  on leaving the vanes, will

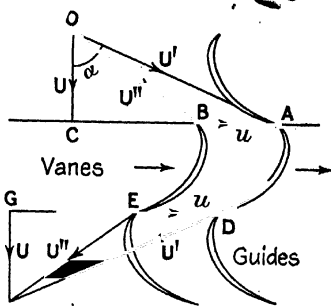


Fig. 27.

be the same as that with which it met the previous guides. The tangential component of the relative velocity of exit, represented by the line  $^{\circ}DG$ , is evidently  $U' \cos \beta$ , or  $U \tan \alpha$ . Adding the resolved parts of the impulse and reaction, and multiplying by  $u$ , we obtain

$$\bullet \quad W = (2U' \cos \beta - u)u/g = (2z - 1)u^2/g, \dots\dots(8)$$

where  $z$  represents, as in the previous case, the velocity-ratio  $U' \cos \beta/u$ , or  $U \tan \alpha/u$ . In the case of a reaction turbine, and in the later stages of an impulse turbine when the nozzles form a complete ring, it is often preferable to express  $z$  in terms of  $U$  and  $\alpha$ , in place of  $U'$  and  $\beta$ .

**116. Mass-Flow, Pressure, and Speed.** The power developed is the product  $MW$  of the work  $W$  per unit mass by the mass-flow  $M$  per unit time. The mass-flow depends chiefly on the areas of the nozzles, and on the initial conditions of pressure, etc., and is nearly independent of the speed and the final pressure. This is obvious in the case of an impulse turbine when the pressure-ratio for the first set of nozzles exceeds the critical value, 0.5457, so that the discharge is independent of the back-pressure. The mass-flow is then proportional to the throat-area of the nozzles, and to  $(P_0/V_0)^{1/2}$ , as shown in the previous chapter, and is quite unaffected by any variation of speed. It is by no means obvious *a priori* that the same result would follow in the case of a reaction turbine when the pressure ratio per stage is very small. But it is found to be almost equally true in practice for any number of stages when the whole pressure range is large, as is usually the case.

If the mass-flow is varied by throttling the initial steam, the initial value of the total heat will remain nearly constant (apart from external loss of heat), and the initial velocity of the steam will be practically unaltered, so that the value of  $W$  in the initial stages will remain nearly the same if the speed is constant. If the final pressure is reduced in the same ratio as the initial pressure, the velocity ratio  $z$  may remain nearly the same throughout the turbine, in which case the values of  $W$  will be little altered, and the gross-power exerted will be nearly proportional to  $M$ . But as a rule the reduction of the final pressure, being limited by the condenser, is much less than that of the initial pressure, so that the velocity-ratio in the later stages is modified. The resulting variations of the power can be calculated even if the speed is altered, provided that sufficient data are available for the dimensions and the effi-

ciencies of the several stages. Methods of doing this will be discussed later. For the present purpose it is sufficient to observe that the mass-flow is nearly independent of the speed, and depends primarily on the state of the steam and the distribution of pressure. If these remain nearly constant, it follows that the variation of power with speed will depend almost entirely on the variation of  $W$ .

**117. The Speed-Power Parabola.** If the work  $W$  as ordinate is plotted against the speed  $u$  as abscissa, for any constant values of  $U$  and  $\alpha$  or  $\beta$ , the curve obtained, in either of the ideal cases above considered, is obviously a simple parabola with its axis vertical, starting from the origin, reaching a maximum at the vertex, and cutting the axis again at an equal distance beyond the vertex. In practice it is usually more convenient to plot the curves with  $1/z$  as abscissa, since  $1/z$  is proportional to  $u$ , and the expressions for  $W$  may be put in the form (see Fig. 29)

$$\text{Ideal Impulse Turbine, } W = U^2 \tan^2 \alpha (2/z - 2/z^2)/g, \dots(4)$$

$$\text{Ideal Reaction Turbine, } W = U^2 \tan^2 \alpha (2/z - 1/z^2)/g. \dots(5)$$

The two curves are precisely similar, but the maximum in the case of the impulse turbine occurs at  $1/z = 1/2$ , and in the case of the reaction turbine at  $1/z = 1$ . The maximum itself is twice as great for the reaction turbine as for the impulse turbine with the same value of the tangential component  $U \tan \alpha$  of the steam-velocity. But the blade-velocity  $u$  at which the maximum is reached is also twice as great.

For any construction, a safe limit of velocity  $u$  is imposed by considerations of mechanical stress. Comparing the two types at the same blade-velocity, the appropriate value of the tangential component of the steam-velocity is twice as great in the case of the impulse turbine when  $z = 2$ , as in the case of the reaction turbine when  $z = 1$ . The work done per stage is also twice as great, being  $2u^2/g$  per unit mass of fluid, in place of  $u^2/g$ . Moreover the wheel of an impulse turbine can be constructed to run safely up to a rim-speed about  $\sqrt{2}$  times as great as the drum of a reaction turbine, which therefore requires in the limit about four times as many stages, or rows of moving blades, as the impulse turbine for the same drop of pressure. This might appear at first sight to be an overwhelming disadvantage of the reaction type, but the reduction of steam-velocity tends to improve the efficiency in some respects, and the drum construction so greatly facilitates the

multiplication of stages that there is really very little to choose in practice between the two types.

In considering how far the ideal formula for  $W$  can apply in practical cases, it is evident that  $W$  must vanish in any case when  $u = 0$ .

In the case of the impulse turbine, where the construction ensures equality of pressure on the two sides of the blade-rim, it is also evident that there can be no impulse on the moving blades when the tangential component of the steam-speed is equal to the blade-speed. It is found in practice that the maximum of  $W$  is nearly midway between these two extremes at  $z = 2$ , except in the case of small machines where the actual flow differs greatly from the ideal conditions assumed. The first half of the curve from  $u = 0$  to the vertex, is the most important in practice, since it is preferable to keep  $u$  on the low side of the maximum. This half of the curve is found to be parabolic within the limits of experimental error. The other half is more difficult to investigate satisfactorily, but nothing is gained by pushing  $u$  beyond the maximum. Reducing  $u$  below the maximum, say from  $1/2$  to  $1/3$  of  $U' \cos \beta$ , reduces the mechanical stress in the ratio of 9 to 4, but it only reduces  $W$  in the ratio of 9 to 8. For this reason the normal blade-speed is frequently in the neighbourhood of  $U'/3$  or even less for small machines.

In the case of the reaction turbine, it is often stated that the maximum efficiency is reached when  $U' = 2u$ , to  $2.5u$ , as in the case of the impulse turbine. This may be true for marine turbines with direct driven propellers if the propeller efficiency is included. But it cannot be true for the turbine by itself, if the expansion is equally divided between the fixed and moving blades. In fact values of  $u$  much greater than  $U'/2$  are commonly employed in reaction-turbines for driving electric generators, but it is seldom worth while to reduce the value of  $z$  below 1.5, because little advantage could be gained thereby, and considerations of mechanical stress are even more important in the drum type than in the wheel type. If the expansion is unequally divided, between fixed and moving blades, with  $z'u$  and  $z''u$  for the tangential components, the expression for  $W$  is

$$W = (z' + z'' - 1) u^2/g, \dots\dots\dots(6)$$

giving a maximum per stage when the mean of  $z'$  and  $z''$  is equal to unity.

**118. Efficiency and Leaving-Loss.** The kinetic efficiency of any stage of a turbine may be defined as the ratio  $W/K$  of the gross work done to the kinetic energy supplied. For a single impulse-wheel, in the ideal case above considered, we have  $K = U'^2/2g$ , and the expression for the efficiency is

$$W/K = (U'^2 - U''^2)/U'^2 = 4(z-1)/z^2 \sec^2 \beta, \dots\dots(7)$$

the maximum value of which is  $\cos^2 \beta$  when  $z = 2$ . This expression, or its equivalent, is often quoted as "the efficiency" of an impulse wheel, but it takes account only of the leaving-loss  $U''^2/2g$ , representing the kinetic energy rejected. In practice, losses due to friction, etc., are generally more important than the leaving-loss, so that the above expression should be regarded rather as representing a limit of efficiency theoretically attainable in the absence of friction and other losses.

A similar, but not identical, expression applies to a single reaction pair, but is without practical significance, because reaction pairs are never used singly. In the case of a series of similar impulse wheels or reaction pairs, when the angles and areas are adjusted so that the initial and final velocities  $U'$  and  $U''$  repeat themselves for each wheel, there is no loss in the absence of friction except at the end of the series. The relative importance of the leaving-loss is reduced in proportion to the number of wheels, whereas the percentage loss due to friction for each wheel is nearly independent of the number of wheels. For this reason the leaving-loss is best treated separately.

Of the other losses, those which vary as the square of the steam-velocity are usually the most important. The percentage loss due to such causes will be independent of the absolute speed for any given value of  $z$  under similar conditions, because  $W$  also varies as the square of the speed when  $z$  is constant. But if  $z$  varies, it appears that the kinetic efficiency  $f'$  must vary with  $z$  in the same way as  $W$ , so far as losses of this type are concerned. It is most important to take account of this in considering the effects of variation in the conditions on the performance of a machine, since small variations of pressure or other conditions may produce large variations of  $z$  in some of the stages. A simple method of applying this relation between  $f'$  and  $z$  will be explained in a later section.

**119. The Power-Consumption Line.** If the mass-flow, or total consumption of steam, in lbs. per sec., or other convenient

units, is plotted as ordinate against the brake horse-power, or shaft horse-power, as abscissa, the curve obtained is nearly a straight line provided that the speed is maintained constant, and that the regulation is effected by throttling. A curve of this kind was first given by Willans (*Proc. Inst. C. E.*, 1893) for a special type of reciprocating engine, but a similar relation has been found to apply to other types of engines, and especially to turbines, within the limits of accuracy of most experimental tests. In the case of a reciprocating engine, the line is appreciably curved if the regulation is effected by varying the cut-off, which tends to improve the efficiency at intermediate loads. Similar small variations occur in the case of turbines according to the type and method of regulation, but the relation is sufficiently close to be of considerable practical use.

The steam consumption  $M_0$  at no load includes leakage, and represents the power required to keep the rotor revolving against the steam-friction, and the friction of bearings, glands etc. If the power-consumption line is straight, the mass-flow  $M$  required at any other load is given by the relation'

$$M = M_0 + m \text{ (B.H.P.)}, \dots\dots\dots(8)$$

where  $m$  is a constant coefficient representing the slope of the line. If  $M$  is in lbs. per hour, the coefficient  $m$  is in lbs. per H.P. hour.

A turbine cannot be "indicated" like a reciprocating engine, but if we assume that the steam required to overcome friction, etc. is the same at all loads, provided that the speed is constant, the quotient  $M/m$  may be regarded as representing the gross power exerted by the steam. The coefficient  $m$  is often treated as being analogous to the consumption per *indicated* horse-power-hour, but this method unduly favours the turbine as compared with the reciprocating engine. The true measure of the indicated power in both cases is the drop of total energy (multiplied by  $M$  and by the appropriate numerical factor), which takes proper account of steam-friction as explained in the next section. See Fig. 28.

## 120. Thermodynamical Equation of Steady Flow.

The general equation of steady flow through a turbine, obtained by the application of the law of conservation of energy, is that already given in Chapter II, section 10, namely,

$$H' - H'' = Q_s + AW'' + A(U''^2 - U'^2)/2g, \dots\dots\dots(9)$$

in which  $H' - H''$  is the actual drop of total heat from the initial to the final state,  $Q_s$  the external *loss* of heat by the fluid, and  $AW''$



the equivalent of the external loss of energy of the fluid in the form of work done by the turbine. The last term, depending on  $U$  represents the excess of the kinetic energy rejected over that supplied. The whole equation may also be interpreted as expressing the fact that the drop of *total energy*  $H - AU^2/2g$  in calories is equal to the sum of the external heat-loss  $Q_x$  and the thermal equivalent of the work done  $AW''$ , per unit mass of fluid.

The effect of internal friction is included in  $H''$ , which represents the actual total heat in the final state. But if the *total energy* rejected with the exhaust steam is measured by observing the rise of temperature of the circulating water in the condenser, the measurement will include  $AU'^2/2g$  in addition to  $H''$ , and a correction for  $U'$  must be made in deducing  $H''$ . The initial value  $H'$  may be obtained from  $P$  and  $T$  if the initial state is one of superheat, as is often the case. If not, the wetness may be estimated with a throttling calorimeter. In either case a correction should be applied for  $U'$  if the initial velocity is appreciable, since the quantity given in the tables is not the total energy but the total heat  $H$ . The corrections for  $U'$  and  $U''$  are generally small, and may often be neglected. The external loss of heat  $Q_x$  may also be regarded as a small correction, especially in the case of large machines.

Assuming that the small corrections for  $U$  and  $Q_x$  are applied, as above indicated, whenever necessary in experimental work, the equation of flow may be employed for theoretical purposes in the simplified form

$$DH = H' - H'' = AW'' = F(H' - H'')_0 = F \times DH_0 \dots (10)$$

In the absence of friction, or external heat loss, or waste of kinetic energy, the maximum work obtainable for given limits of pressure is the equivalent of the adiabatic heat-drop  $(H' - H'')_0$ . Thus, if the relative efficiency  $F$  is defined as in Chapter IX, we can estimate  $F$  and  $H''$  from  $AW''$ , or *vice versa*,  $F$  and  $AW''$  from  $H''$ , or  $AW''$  and  $H''$  from  $F$ , according to the available data, as illustrated in the following examples.

**121. Example of Marine Turbine.** The turbines of the *Mauretania* are said to have developed 34,000 shaft horse-power each, at 190 revs./min. with a consumption of 12.8 lbs. per horse-power-hour, excluding auxiliaries.

Neglecting all corrections,  $DE = AW = 115.0$  cal. C.

Taking the initial pressure as 165 lbs. abs., and the final pressure

as 1 lb. abs., and the initial state as dry saturated, the adiabatic heat-drop is 180.9 cal. C., giving relative efficiency  $F = 0.686$ .

It is not clearly stated how the shaft horse-power was measured, and it is uncertain how much of the bearing friction was included. Allowing 3 per cent. for bearing, gland, and dummy friction of the turbine, the nett work done by the steam per lb. in thermal units would be  $AW = 118.5$  cal. C., giving  $F = 0.655$  for the indicated relative efficiency.

The drop of total energy of the steam being 118.5 cal. C., the actual drop of total heat in the final state is obtained by adding a correction  $AU''^2/2g$  for the kinetic energy rejected. To estimate the final velocity  $U''$ , we have  $U''^2 = U^2 + (z - 1)^2 u^2$ , where

$$U = 144MV/X \text{ ft./sec.}$$

From the dimensions of the turbine,  $X = 11200 \text{ in.}^2$  for the last expansion,  $u = 134$  at 190 revs., and  $M = 116 \text{ lbs./sec.}$  Taking 1.3 lbs. abs. for the exit pressure allowing for condenser-drop, and  $DH = 120$ , the final value of  $H''$  is 547.6, which gives the final volume  $V'' = 229.6$ , whence  $U = 343 \text{ ft./sec.}$  Taking  $z = 2$ , the small correction for  $u$  gives  $U'' = 368 \text{ ft./sec.}$ , whence the kinetic energy rejected is equivalent to 1.5 cal. C., giving the actual heat-drop  $DH = 120.0$ . The correction in this instance is small on account of the low speed, but it may exceed 5 per cent. at high speeds. It does not affect the indicated efficiency, but only the final state and volume. The correction makes a difference of 1 or 2 per cent. at most in the value of  $V''$ , so that, unless very accurate values of  $V$  are required, it is usually best to calculate  $DH$  directly from  $z$  or  $AW''$ , without applying any correction for  $U''$ , especially when  $U''$  is nearly the same at the end of each expansion, so that it does not affect the values of  $DH$ , but only comes in as a small constant correction in the absolute value of  $H''$ .

Similar considerations apply to the external heat-loss  $Q_s$ , which is usually small, but always very uncertain. The absolute values of  $H''$  and  $V''$  as deduced from  $H'$  and  $AW''$ , require a small correction for  $Q_s$ . Similarly if the total energy  $H'' + AU''^2/2g$  is measured, a correction for  $Q_s$  should be applied if possible in deducing  $AW''$ . But any effect of heat-loss on the efficiency is automatically included in the values of  $F$  and  $AW''$  as ordinarily measured. If, therefore, the object of the investigation is to calculate the effect of different conditions on the efficiency, starting with some value of  $F$  experimentally determined under normal

conditions of running, it is often best to ignore  $Q_{\infty}$ , on the principle of the independence of small corrections, and to work with values of  $DH$  deduced from  $AW''$ , since this cannot introduce any material error in the *relative* values of the efficiency if  $M$  is constant.

\* In the case of marine turbines, there is often considerable uncertainty in the estimation of  $F$  and  $AW''$  owing to the difficulty of measuring the steam-feed and the power. Some of the steam is used for driving auxiliaries, the exhaust from which may be partly employed for heating the feed, the residue being taken through the low pressure turbine. Another source of uncertainty is leakage past the dummy or balancing pistons. The amount of such leakage is seldom known with any approach to accuracy. The mass-flow  $M$ , instead of being uniform throughout the turbine, is different in different parts, especially if the auxiliary exhaust is unequally distributed between two turbines in order to balance the propellers on either side of the ship.

Such variations of  $M$  in different parts of a turbine can often be estimated, without actual measurement of the leakage or auxiliary exhaust, by a method explained in a later chapter, provided that full details of the dimensions of the turbine are known, and that the pressure distribution is carefully observed under the actual conditions of running. Unfortunately the required data are seldom available in published tests.

As a rough illustration of the order of magnitude of the corrections involved, we may suppose that auxiliary steam amounting to 1.5 lbs. per horse-power-hour was taken through part of the low pressure turbine of the *Mauretania* in the trials quoted, and that the heat-drop of this part of the steam was half the total drop  $DH$ . The flow through the L.P. turbine being increased in the ratio 13.8/12.8, neglecting all other corrections, the value of  $DH$  must be reduced in the ratio 12.8/13.05, or from 115 to 108.4 cal. C., assuming that the effect of the auxiliary exhaust was included in the 84,000 H.P. This would reduce  $F$  from 0.686 to 0.60. It is evident that such corrections may be of material importance, but as previously remarked, they cannot be satisfactorily applied unless full data of the dimensions and pressure distribution are available. It would appear from the fuller details given in Chapter XVI, that the auxiliary exhaust was *not* in fact utilised in this way in the L.P. turbine of the *Mauretania*, though this was common practice in battleships of the Dreadnought class, the turbines of which were specially designed for the purpose.

**122. Example of De Laval Turbine.** As an example of a different kind we may take the single impulse wheel of a De Laval turbine with a set of expanding nozzles of the type discussed in the last chapter. Assuming that the expansion in the nozzles is from 150 lbs. (dry sat.) to 2 lbs. abs., the adiabatic heat-drop for saturated steam would be 158.2 cals. C. Taking the loss in the nozzles at 15 per cent., of which about half would be due to super-saturation, there would remain a heat-drop of 134.5 cals. C, giving a velocity  $U' = 3481$  ft./sec.

In the ideal case, assuming no loss in the wheel, if the nozzles make an angle  $\beta = 20^\circ$  with the plane of the wheel, the maximum wheel-efficiency attainable would be  $\cos^2 \beta = 0.883$ , and the leaving-loss 11.7 per cent. of 134.5 cals., or 15.7 cals. But this would require a rim velocity  $u = U' \cos \beta = 1635$  ft./sec., which would be dangerously high.

Supposing the rim velocity reduced to  $u = U'/3 = 1160$  ft./sec., the mechanical stress would be reduced to one half, the velocity ratio  $z$ , or  $U' \cos \beta / u$ , would be increased from 2 to 2.820, and the limiting value of the kinetic efficiency in the absence of all frictional losses would be reduced to

$$W/K = 4(z - 1) \cos^2 \beta / z^2 = 0.808. \dots\dots\dots(11)$$

The leaving loss would be increased to 19.2 per cent. of  $K$ , or 25.8 cals. C. This might appear at first sight a serious reduction of efficiency, but, in point of fact, the other losses in the wheel reduce the leaving loss to less than half this value. The losses in the wheel, and the actual leaving velocity, can be estimated if the consumption is given.

Supposing that the observed consumption is 16 lbs. per brake horse-power hour, equivalent to an effective heat-drop of 88.4 cals. C., if we add a correction of 2 per cent. for gear and bearing friction, we obtain 90.2 cals. for the equivalent of the nett work done on the wheel per lb. of steam, giving  $90.2/134.5 = 0.671$  for the wheel-efficiency, and

$$F = 0.85 \times 0.671 = 0.570, \dots\dots\dots(12)$$

for the indicated relative efficiency of the wheel and nozzle combined.

In addition to the loss due to gear and bearing friction, there is a more serious loss due to steam-friction, which must be allowed for in estimating the gross work  $W$  done on the wheel by the steam in the formula for the kinetic efficiency  $W/K$ . The nozzles occupy a

small part only of the circumference of the wheel, the greater part of which is running idle in the partial vacuum, and acts like a centrifugal fan, wasting power by setting the steam in circulation. The power wasted in this way varies as the cube of the revolutions, and as the density of the medium. In the case of a single wheel the leakage is negligible, and the loss due to fan-action can be estimated with some degree of precision by observing the total consumption  $M_0$  required to run the wheel at no load with normal speed and vacuum. If  $M_1$  is the consumption at normal load corresponding to the observed B.H.P., the power required at no load is  $M_0/(M_1 - M_0)$  of the B.H.P., or  $M_0/m$ , according to the linear law, § 119.

In the present case, if the power required at no load is found to be 10 per cent. of the B.H.P. at full load, the gross work done by the steam on the wheel may be estimated as equivalent to

$$88.4 \times 1.10 = 97.2 \text{ cal. C.}$$

which gives for the actual kinetic efficiency of the wheel, considered separately,

$$W/K = 97.2/184.5 = 0.527. \dots\dots\dots(18)$$

But the power wasted in fan-action does not appear, either at the shaft, or in the heat-drop, and cannot fairly be included in the "indicated" efficiency, as is frequently assumed.

In order to estimate the relative velocity  $U_r''$  with which the steam leaves the wheel, we have to substitute  $AW = 97.2$  in the general formula (1) for  $W$  in terms of the relative velocities. Since  $U_r' \cos \beta' = U' \cos \beta - u = 3271 - 1160 = 2111 \text{ ft./sec.}$ , the work done by the impulse is equivalent to

$$2111 \times 1160/32.19 \times 1400 = 54.3 \text{ cal. C.}$$

The work done by the reaction is equivalent to

$$97.2 - 54.3 = 42.9 \text{ cal. C.}$$

Whence  $U_r'' \cos \beta'' = 42.9/54.3$  of  $2111 = 1668 \text{ ft./sec.}$  The tangential component of the absolute leaving velocity  $U''$  is evidently  $1668 - 1160 = 508 \text{ ft./sec.}$  The axial component of  $U''$  is

$$U_r'' \sin \beta'' = 1668/2111 \text{ of } U' \sin \beta = 941 \text{ ft./sec.,}$$

whence  $U'' = 1069 \text{ ft./sec.}$  The thermal equivalent of the actual leaving-loss is  $(1069/800)^2 = 12.7 \text{ cal. C.}$

The drop of kinetic energy in passing through the wheel, represented by  $(U'^2 - U''^2)/2g$ , is equivalent to  $121.8 \text{ cal. C.}$ , and is equal to the sum of the work done,  $97.2$ , and the energy wasted,  $24.6 \text{ cal. C.}$ , in the wheel.

We are now in a position to make a tabular summary of the various losses incurred, which work out as follows:

Summary of losses in De Laval turbine.

Loss in nozzles ...	23.7	cal. C. =	15	per cent.
Loss in blade-rim ...	24.6	" =	15.5	"
Leaving loss ...	12.7	" =	8.0	"
Loss due to fan-action ...	7.0	" =	4.4	"
Gear and bearing friction	1.8	" =	1.2	"
Equivalent of B.H.P. ...	88.4	" =	55.9	"
Adiabatic heat-drop ...	158.2	" • =	100.0	"

The actual distribution of the losses will vary in different cases, and under different conditions of running, but the above analysis seems to afford a fair representation of the conditions assumed in the work. The relatively large losses in the nozzles and blade-rim result chiefly from taking the full pressure-drop on a single wheel of small size. They can be reduced in large machines by dividing the pressure-drop between several wheels and nozzles in series, but there is not much to be gained by the additional complication for low powers.

The losses in the blade-rim may be attributed partly to the breaking up of the steam jet by the inlet edges of the blades, which cannot be infinitely sharp, and require periodical renewal on account of wear at such high steam velocities. They are also partly due to the spreading of the jet occasioned by the driving pressure on the blades, which in this case would be of the same order of magnitude as the absolute pressure of the surrounding vacuum, and would necessarily cause reduction of velocity and distortion of the flow. Such details must be kept in view by the inventor and designer, but it is seldom desirable to take account of all these separate causes of loss in the thermodynamical theory. In the case of an impulse turbine, it is possible to take the nozzle losses separately, but it is generally sufficient to include them with the wheel losses by taking a mean effective value of the velocity-ratio  $\alpha$  for calculating the kinetic efficiency, or the gross work, corresponding to the speed-power parabola. Additional losses due to leakage, fan-action, etc., are included in the brake-efficiency.

**123. Example of Turbo-Electric Generator.** A turbine driving an electric generator affords special facilities for test under variable load at constant speed. The curves shown in the annexed

Fig. 28 illustrate the relation between mass-flow  $M$  in lbs. per sec. taken as ordinate, and total power in kilowatts  $KW$  taken as abscissa, corrected for the known efficiency of the electric generator, so as to give the equivalent of the shaft horse-power of the turbine at each load. The scale at the base indicates thousands of kilowatts approximately, but the actual observations have been slightly reduced to afford a more convenient comparison between two different types of machine. The horizontal crosses (+) represent observations with a reaction turbine of the Parsons type, the diagonal crosses (x) represent similar observations with an impulse turbine of the Curtis-Rateau type.

In the case of the reaction turbine the regulation for constant

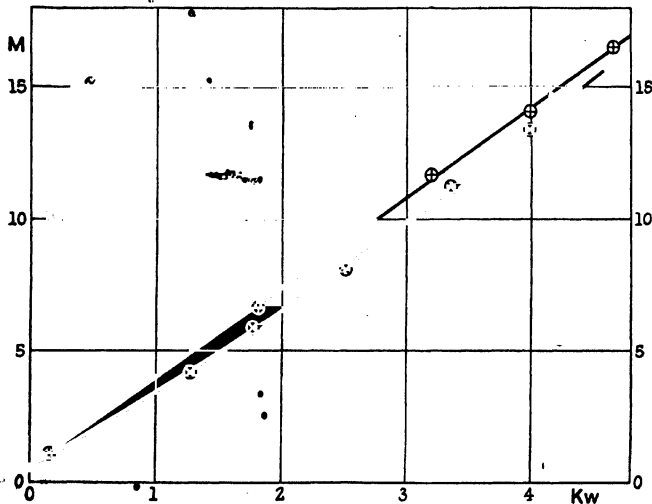


Fig. 28. Power-Consumption Lines of Turbo-Generators.

speed was effected by throttling, and the points lie nearly on a straight line drawn through the highest and lowest observations. The steam-feed was measured at no load with the generator excited, and the abscissa of the lowest point represents the power required to drive the generator under this condition at normal speed, estimated from the known losses in the generator. The steam required to run the turbine by itself under no load at normal speed can be estimated in this case with some degree of precision by producing the straight line to cut the axis, and is seen to be about

8 per cent. of the steam required at maximum load. This includes bearing friction, and shows that the steam friction must be very small at the low pressure.

In the case of the impulse turbine the load was varied by cutting out nozzles, which is analogous to varying the cut-off in the case of a reciprocating engine. The steam at no load was not recorded, and could not have been measured without throttling, but was probably much the same as for the reaction turbine. The power-consumption line is seen to be distinctly curved with this method of regulation, as in the analogous case of the reciprocating engine when the cut-off is varied.

The small deviations of the individual observations from the smooth curves appear to depend on accidental variations in the conditions of superheat, pressure, and vacuum, and could no doubt be corrected if sufficient data were available. The systematic difference between the two machines in respect of consumption per kilowatt hour, or mass-flow per kilowatt, appears to be due chiefly to the fact that the impulse turbine was tested with a superheat more than  $100^{\circ}$  F. higher than the reaction turbine. This not only improves the consumption by reducing the density, but also improves the relative efficiency by eliminating loss due to super-saturation, as explained in the next chapter. The improvement does not appear to be due to any great inherent superiority of one type of machine, or one method of regulation, over the other, but it has the advantage for the present purpose of separating the curves sufficiently to avoid confusion.

In addition to the effect of superheat, the total efficiency, in terms of consumption per kilowatt-hour, or the absolute thermal efficiency, in terms of the ratio of the work done to the heat supplied, depends very greatly on the ability of the machine to utilise the highest available vacuum without excessive leaving-loss. Improving the vacuum always improves the performance, but the full theoretical advantage cannot be obtained unless sufficient area is provided for the increased volume. The record for axial flow machines is at present held by a reaction turbine with a double flow for the later stages of the low pressure cylinder, but the radial flow turbine of Ljungström is credited with a still better performance, due in part to its natural ability to utilise a very high vacuum.

For the same reason, improving the vacuum beyond that for which the machine is designed, invariably reduces the relative efficiency  $F$ , whereas reducing the vacuum improves  $F$  to some



extent. It is obvious that  $F$  could not remain constant unless the dimensions were altered to suit the vacuum. The actual effect of any change in the vacuum can be calculated in any case if the dimensions of the machine are known. An example of a possible method of doing this will be given in Chapter XV.

**124. Compound Impulse Wheels** (often called "Curtis," or "Velocity-compounded," or "Velocity" wheels). When a low ratio of blade- to steam-velocity is a primary consideration, wheels with two or more rings of blades are employed. The steam rejected from the first ring with tangential velocity  $(z - 2)u$ , is received by a fixed ring of guide-blades suitably shaped to reverse the tangential component and direct the steam back on to the second ring of moving blades, which effect a further reduction of the tangential component to  $(z - 4)u$ . The addition of a third ring would leave the tangential component at  $(z - 6)u$ , and so on. The leaving-loss need not exceed the theoretical minimum  $\sin^2 \beta$ , even if  $z$  is large. But owing to the length of path, and to the cumulative effects of imperfect flow, the efficiency of a double or triple wheel can never be so good as that of a simple wheel with a suitable velocity-ratio. It appears from experimental tests that the maximum efficiencies of wheels with one, two, and three rows of blades, under similar conditions, are approximately in the ratio of the numbers, 6, 5, and 4, and are attained with values of  $z$  equal to 2, 4, and 7 nearly\*. According to these figures, a double wheel would replace four simple wheels at the same blade-velocity, but would give little more than three times the work of one. A triple wheel would replace about 12 simple wheels, but would only give the same work as eight. If efficiency were the only consideration, compound wheels would not be employed; but they possess great advantages when economy of space or cost is essential, especially if fuel is cheap, and a low blade-speed is required, as in marine work. They are also frequently employed in the first stage of expansion with high-pressure or superheated steam, in order to obtain a large drop of pressure and temperature in the first nozzle, so as to reduce the strain and distortion of the casing. The thermodynamical theory is practically the same for a compound wheel as for a simple wheel, but the appropriate values of the heat-drop and efficiency will be different, as already indicated.

\* Deduced from figures given by K. Baumann (*Journ. Inst. Elect. Eng.*, Vol. 49, p. 828, 1912).

**125. The Multistage Impulse Turbine.** In order to avoid excessive *steam-velocities*, it is necessary to divide the available pressure range between a series of nozzles and wheels. Each wheel runs in a separate chamber throughout which the pressure is nearly uniform. The nozzles are fixed in the partitions between the chambers, and are represented by a complete ring of guide-blades in the later stages. The pressure at the exit from one nozzle is the initial pressure for the next nozzle, and the areas of successive nozzles are adjusted to suit the volume by the condition  $X/M = kV/U$ . The velocity generated in any given nozzle is determined primarily by the pressure-drop between adjacent chambers, but it is desirable to allow for friction in estimating the final values of  $H$  and  $V$  in each stage, which serve as the initial values for the next nozzle. In addition to reducing the steam-velocity to a reasonable figure, the multistage arrangement possesses the advantage that work spent in fluid friction in the early stages of the expansion is not completely wasted, but is partly utilised by reconversion in the later stages. The velocity of the steam rejected by one wheel may also be partly utilised by "carry-over" in the next nozzle, or guide-ring, so that the loss in the later stages is reduced.

The number of stages into which a given heat-drop must be divided to suit a given blade velocity  $u$ , is readily estimated from the consideration that  $U'$  should not exceed  $3u$  for a simple impulse wheel. Thus if the pressure range is 165 to 1 lb., and  $u = 400$  ft./sec.,  $U'$  may be 1200, corresponding to a heat-drop of 16 cals. The available heat-drop is 181 cals. so that 10 or 11 simple wheels would suffice, allowing a margin for loss of steam velocity. Similarly if  $u = 200$ , the same number of stages each with a compound wheel of two rings would be sufficient; but 40 simple wheels would be required. As a rule the given data are, the pressure range, the revolutions, and the power; and the required conditions may be satisfied in many different ways with almost equal efficiency. The design adopted is frequently determined by cost of fuel or construction, or by mechanical considerations which are beyond the scope of the present work. The properties of steam are required chiefly in determining the choice of suitable areas for the nozzles corresponding to the subdivision of the heat-drop, and in the estimation of the efficiencies of different arrangements, which afford good illustrations of the methods of using the tables.

**126. Flow through an "Expansion" in a Reaction Turbine.** The number of separate stages, or pairs of fixed and moving blades, in a reaction turbine is rarely less than 50 and often exceeds 200. These are grouped in "expansions," each consisting of several stages with the same blade-height  $x$  and annular area  $X$ . Each expansion may conveniently be treated as a single unit in calculating the flow when the dimensions are given. In some cases the blade-angle  $\alpha$  is varied throughout the expansion so as to keep either the exit velocity  $U'$ , or the tangential component  $U \tan \alpha$ , constant. But more often the blade-angle is the same throughout, and the exit velocity  $U'$  increases with the volume. It is sufficient in either case to take a mean value of  $\tan \alpha$ , or a mean value of the velocity ratio  $z$ , so that the solution of the problem depends on selecting an appropriate method of finding the mean effective value of  $z$  in any case for the whole expansion.

In passing from one expansion to the next, the annular area  $X$  is increased, so as to allow for the increase of  $V$ , and to bring the velocity back as nearly as possible to the same value at the beginning of each expansion. The increase of kinetic energy during the expansion being thus rejected and reconverted into heat, the equation of steady flow for the complete expansion reduces to the form

$$H' - H'' = AW'', \dots\dots\dots(14)$$

if the external heat-loss  $Q_e$  is neglected as previously explained. The actual heat-drop from the beginning of one expansion to the beginning of the next is the equivalent of the nett work  $W''$  done on the rotor between the same limits, making allowance for all *internal* losses, such as leakage, or steam-friction, or fan-action, but not including losses external to the expansion, such as bearing friction, or dummy leakage.

The expression previously given for the gross work  $AW'$  in terms of  $z$ , may be held to include nozzle and blade losses, which vary as the square of the steam-speed and reduce the effective value of  $z$ . It may be applied to an expansion of  $N$  pairs, or stages, by writing it in the form

$$AW' = (2z_m - 1) Nu^3/Jg, \dots\dots\dots(15)$$

where  $z_m$  is the arithmetic mean of the values of  $z$  for the separate stages. This expression for  $AW'$  gives the gross work per unit mass done by that portion of the steam which pursues the ideal path through the blades. It does not apply to the fraction that misses the blades owing to lateral spreading, or that leaks over the blade-

tips without adding anything to the work or the heat-drop, and it takes no account of work wasted in friction between the steam and the rotor. For these reasons the net work  $W''$  per unit mass of the *total quantity* of steam passing through the expansion is necessarily less than the gross work  $W'$  calculated from  $z$ .

The ratio  $W''/W'$  will be called the "Reaction Efficiency," and will be denoted by  $f''$ . It may be regarded as representing the proportion of the theoretical reaction  $W'$  due to the velocity which is actually realised as work on the shaft. The expression for the heat-drop per expansion in terms of  $z$  and  $f''$  is

$$H' - H'' = f'' (2z_m - 1) Nu^2/Jg. \dots\dots\dots(16)$$

The reaction efficiency  $f''$  will evidently be the same for the separate stages of an expansion in so far as the dimensions remain constant, but will vary systematically from one expansion to another when the dimensions are varied. It is convenient to separate the losses included in  $f''$  from those included in the kinetic efficiency  $f'$ , because they depend on different conditions, and vary in a different manner. The systematic variation of the reaction efficiency  $f''$ , as depending on leakage, ~~etc.~~ may most simply be represented by a formula of the type  $f_1'' - l''/x$ , where  $x$  is the blade-height and  $l''$  a constant depending on the effective leakage-clearance. The term  $f_1''$  includes other effects of distortion of flow, and will have different values for different types of wheel, and for the case of partial as against complete peripheral admission. The kinetic efficiency on the other hand, depends chiefly on the velocity-ratio  $z$ , as previously indicated, and is, in the main, independent of the absolute velocity and of the linear dimensions. It is necessary to have some fairly simple expressions for the systematic variations of these coefficients in order to be able to compare theory with experiment and to deduce the probable effects of different conditions on the performance.

**127. Kinetic Efficiency and Available Energy.** In a reaction turbine, the kinetic efficiency for a single stage is related to the available energy  $aVdP$  by the equation

$$f'aVdP = (2z - 1) u^2/Jg = U^2 \tan^2 \alpha (2/z - 1/z^2)/Jg. \dots(17)$$

When the pressure-drop  $dP$  per stage is small, it is sufficient to take the mean value of  $V$  in the expression  $aVdP$  without integration. The axial velocity  $U$  will vary directly as  $V$  from one stage to another in the same expansion in virtue of the relation

$U = kMV/X$ . If the blade-angles are gauged so that  $U \tan \alpha$  and  $z$  are constant, we may assume that  $f'$  will also be constant, and that  $dP$  will vary inversely as  $V$ . If on the other hand, the blade-angle  $\alpha$  is constant, as is usually the case, the velocity-ratio  $z$  will vary directly as  $V$ , and  $f'$  will vary from one stage to another in a systematic manner.

It is necessary in any case to have a simple rule for defining the mean effective value of  $z$ , since the exact value of the discharge angle  $\alpha$  cannot be predicted with any certainty from the form of the blades. For this purpose we shall assume (1) that the nozzle and blade-losses vary directly as the square of the tangential component of the steam-velocity for any given value of  $z$ , that is to say, in the same manner as  $W'$  when  $z$  is constant, in which case  $f'$  will be constant, and (2) that  $f'$  varies in the same way as  $W'$  when  $U \tan \alpha$  is constant. These assumptions give the simplest relations consistent with the main experimental facts, though they do not appear to be capable of formal proof for every type of blade and variety of condition.

Adopting these assumptions as a working hypothesis, we have the following simple relations for finding  $f'$  and  $z$  in any case

$$f' = f'_1 (2z - 1)/z^2, \quad \text{and} \quad f'_1 \int aV dP = Nz_m^2 u^2 / Jg, \dots (18)$$

where  $f'_1$  is the maximum value of  $f'$  when  $z = 1$ , and is a constant to be determined by experiment for each particular type of blade or wheel. The first relation gives the variation of  $f'$  in terms of  $z$ , and the second relation defines the mean effective value of  $z$ . When  $z$  and  $f'$  are variable, the mean value of  $f'$  for any expansion may be taken as that corresponding to the mean effective value of  $z$ .

In the case of an impulse turbine, by similar reasoning, a similar relation will apply for defining the mean effective value of  $z$  for each wheel including both nozzle and blade-losses, so far as these vary as the square of the steam-speed. But owing to the difference between the expressions for  $W'$  in the case of impulse and reaction turbines respectively, the maximum value of  $f'$  denoted in this case by  $f'_2$ , occurs at  $z = 2$ . Thus we have

$$f'/f'_2 = 4(z - 1)/z^2, \quad \text{and} \quad f'_2 \int aV dP = z^2 u^2 / 2Jg, \dots (19)$$

where  $zu$  represents the effective tangential component of the steam-speed. Since the two types of turbine are essentially similar as regards variation of kinetic efficiency with velocity-ratio, especially in the later stages when the peripheral admission is

complete, results deduced for one will apply equally to the other so far as they depend on these relations.

In the case of the reaction turbine, a simple and useful expression for the pressure-drop per stage, or per expansion, is obtained by substituting for  $V$  in  $aVdP$  from the relation  $V = UX/kM$  with  $U = uz/\tan \alpha$ , thus,

$$\text{Pressure-drop per stage*}, dP = Muz \tan \alpha / f_1' gX, \dots\dots\dots(20)$$

$$\text{Pressure-drop per expansion*}, P' - P'' = NMuz_m \tan \alpha / f_1' gX, \quad (21)$$

where  $z_m$  represents the mean effective value of  $z$ , as in the corresponding formula for the heat-drop, when the blade-angle is constant. In the case when  $z$  is constant and  $\alpha$  is varied, the same formula applies with the arithmetic mean value of  $\tan \alpha$ . The two cases are equivalent, to the order of approximation here attempted, and give the same values both for the heat-drop and the pressure-drop, provided that the mean value of  $z$  or  $\tan \alpha$  in either case is equal to the constant value in the other. These appear to be the simplest formulae capable of taking account of all the primary factors of the problem in a consistent manner, and are readily applied to the solution of any special case when sufficient data are available. It might seem at first sight as though the expression defining the mean effective value of  $z$  were too simple to be true, but it evidently fits the fundamental fact that the mass-flow is practically independent of the speed. If  $M$  is constant,  $zu$  cannot vary without corresponding variations in  $aVdP$ . These and other points of correspondence with experiment serve as indirect means of verifying the working hypothesis. The observed variation of  $f'$  with speed also affords qualitative verification.

### 128. Variation of the Complete Stage-Efficiency $f$ .

The variation of  $f$  with velocity-ratio  $z$  will be similar to that of the kinetic efficiency  $f'$ , but the absolute value of  $f$ , being equal to the product  $f'f''$ , will generally increase in the later stages owing to the systematic variation of  $f''$ . The general nature of the variation is illustrated in the annexed Fig. 29.

In plotting the relation between the kinetic efficiency  $f'$  and the velocity-ratio  $z$ , it is best to take the reciprocal  $1/z$  as the abscissa, because the curve then becomes a simple parabola, namely  $f' = 4f_1'(1/z - (1/z)^2)$ , with its axis vertical, and with its vertex

\* These expressions assume that  $X$  is measured in sq. in. on the F.P.C. or F.P.F. systems, and in sq. cm. on the K.M.C. system.

at  $1/z = 0.5$ , in the case of the impulse turbine. In the case of the reaction turbine the same curve applies, but the values of  $1/z$  are all doubled, so that the maximum occurs at  $1/z = 1$ . The value of the constant  $f_2'$  for the curve marked  $f'$  in the figure is taken as 0.85. The constant term  $f_1''$  in the expression for  $f''$  is taken as 0.95. The variable term  $l''/x$  is taken as 0.0084 for a typical low-pressure blade, and as 0.126 for a high-pressure blade, assuming the respective blade-heights to be in the ratio 15/1. The two lower curves represent the resulting variation of  $f$  for the two cases considered. The low-pressure wheel has a maximum efficiency of 80 per cent. (which is probably about the highest attainable) at

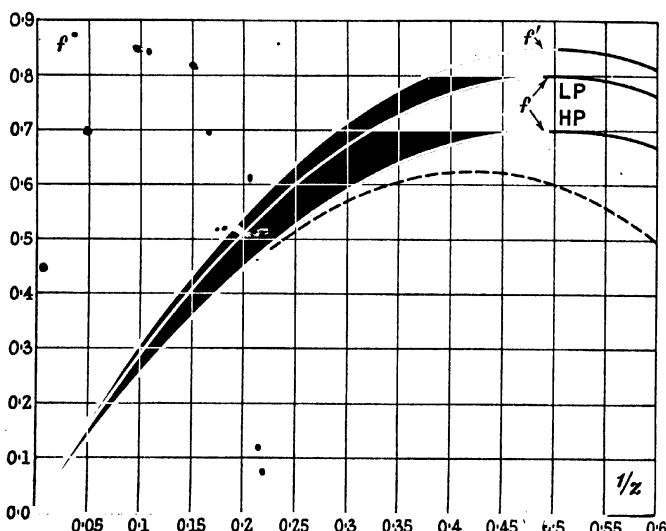


Fig. 2b. Variation of Efficiency (and Power) with Speed-ratio.

$z = 2$ , or  $1/z = 0.5$ , but the wheel would be run at a lower speed in usual practice, owing to the great saving in mechanical stress, with little loss of efficiency. This curve happens to agree exactly with one given by Baumann (*Journ. Elect. Eng.*, 48, p. 782, 1911), except that his curve is plotted against the ratio,  $u/c$ , or  $\cos \beta/z$ , of the blade-velocity to the full steam-velocity, and therefore shows a maximum at  $u/c = (\cos \beta)/2$  instead of at  $1/2$ . Baumann's curve is stated to represent "a fair average of test results actually being obtained in the low-pressure part of modern Rateau turbines." It appears to afford a good general confirmation of the theory here

proposed, but no details of the tests are given, so that it is difficult to say how far the correspondence is real. The lower curve in Fig. 29, representing the high-pressure wheel, has a maximum of 70 per cent., but is otherwise exactly similar to the other curves.

The verification here attempted appears to show that the variation of efficiency with speed can be represented within the limits of experimental error by a parabolic curve having its maximum at the theoretical value of  $z$ . This cannot be exactly true if the loss due to a fan-action varies as the cube of the speed, unless there is some other compensating effect, tending to raise the point at which the maximum occurs. The effect on the reaction efficiency of a loss varying as the cube of the speed is indicated in the last figure on an exaggerated scale by the broken curve. This is obtained from the lowest curve in the figure by deducting a loss equal to 10 per cent. at  $1/z = 0.5$ , and varying as the cube of the speed at other values of  $1/z$ . The effect in this case is to lower the position of the maximum to  $1/z = 0.42$ , but the form of the curve is still so nearly parabolic that it would be difficult to distinguish it experimentally from a true parabola. The lowering of the maximum is very marked in small machines, such as the 5 or 10 H.P. De Laval, which give the maximum B.H.P. at rim-velocities well below the theoretical, but it would be difficult to detect in large multistage machines, say of 5000 H.P., where it would be impracticable to analyse the losses very accurately for the separate wheels, or to vary the speed over a wide range without upsetting the pressure distribution. It is also possible that the blades may be shaped so as to increase the reaction, which would have the effect of raising the apparent position of the maximum, and is sometimes said to improve the efficiency.

In many cases the effect of fan-action is comparatively unimportant, and may be neglected unless the effect of variation of speed is in question. But it is of interest to consider the cases in which it may become important. It is generally agreed that the effect varies for a given wheel as the cube of the speed and as the density of the medium, but there is much conflict of opinion, and even of experimental evidence, on minor points. Some of the formulae proposed are obviously inadmissible, while others are more complicated than is justified by the nature of the evidence.

**129. Expression for the Loss due to Fan-Action.** Fan-action, or wheel-friction as it is often called, appears to be more



important in the case of the impulse wheel at high pressures than in the case of the reaction drum, where tip-leakage is a more serious source of trouble. The effect depends on so many conditions, such as the fineness of the clearances and the shrouding of the blades, that it is impossible to give a complete formula applicable to all cases. The following expression is intended merely to give a general idea of the order of magnitude of the loss in the case of a wheel when the clearances are reasonably fine. It is founded on the assumption that the loss is proportional to the density of the medium, to the area of the effective surface and to the cube of the velocity of each part relative to the casing.

$$\text{Wheel-friction} = (3r^2 + 30rx)(u/1000)^3/V, \text{ Horse-power, } \dots(22)$$

where  $r$  is the mean radius of the blade-rim, and  $x$  the nozzle-height in inches,  $u$  the mean blade-velocity in ft./sec., and  $V$  the volume in cb. ft./lb. The term  $3r^2$  represents the effect of the surface of the disc, the term  $30rx$  that of the blade-rim. If the lateral surface of the blade-rim were smooth like the disc, the numerical coefficient of  $rx$  would, in the limit for short blades, be five-times that of  $r^2$  on the assumptions made. The surface of the blade-rim being discontinuous, this coefficient cannot be less than five times the first, but may be as great as 20 times or more, especially for compound wheels. The term representing the effect of the disc is the larger of the two at high pressures when the blades are short, but becomes relatively negligible at low pressures on account of the diminution of density, and increase of blade-height.

The relative importance of either is readily expressed in terms of the theoretical maximum power,  $2Mu^2/g$  ft. lbs./sec. at  $z = 2$ , for a single impulse wheel. The ratio comes out  $0.0080 \tan \alpha/\eta$ , for the blade-rim friction, and  $0.0008r \tan \alpha/\eta x$ , for the disc-friction (by substituting  $M = UX/144V$ ,  $U = 2u/\tan \alpha$ , and  $X = \eta 2\pi rx$ ), where  $\eta$  is the arc of admission expressed as a fraction of the whole circumference when the admission is partial, and is equal to unity when the admission is complete.

According to the expression  $0.0080 \tan \alpha/\eta$  for the effect of the blade-rim friction on the efficiency, the reduction of efficiency would be of the order of 1 per cent. only for the low pressure wheels at maximum power, and would be much the same for all, so long as the admission was complete, and the angle  $\alpha$  was not varied. The importance of this term would increase in the case of the high pressure wheels with partial admission, especially if  $\tan \alpha$  were

increased, as is often the case. The effect of the disc-friction would be of the same order of magnitude as that of the blade-rim for intermediate wheels when  $r = 10x$ , and would increase in a similar manner for the high pressure wheels, except that it could be reduced by reduction of  $r$ . It is generally agreed to be an advantage, so far as wheel-friction is concerned, to reduce the diameter of the high pressure wheels. This was often done in the earlier types, but has the disadvantage of increasing the number of wheels required, and has been abandoned in most of the later types in favour of a nearly uniform diameter, which is mechanically preferable.

It would appear to be unnecessary to take account of wheel-friction in the low pressure stages, as the resulting distortion of the efficiency curve would be too small to detect. But it would be best for the sake of consistency to represent it throughout the turbine by a systematic variation of the type  $(1 + r/10x) \tan \alpha/\eta$  per cent. in  $f''$ , provided that the speed were uniform and constant; and to allow for variation of speed, if the effect of speed were the object of enquiry.

In the case of the reaction turbine, since the admission is always complete, the effect could probably be included with sufficient accuracy in an expression of the type  $f_1'' - l''/x$ , as previously suggested. But the effect of tip-leakage is here the most important, and the constant  $f_1''$  would approximate closely to unity at low speeds, owing to the absence of disc-friction.

There does not seem to be any satisfactory evidence that the effect of wheel-friction is proportionately greater in small machines than in large, or that it varies as the cube of the angular velocity as opposed to the linear velocity. Small machines of the axial flow type undoubtedly suffer from the excessive curvature of the blade-path, which leads to distortion of flow at high angular velocities, but this cannot fairly be debited to wheel-friction.

Although it is not possible in a formula of this kind to give exact values of the coefficients to suit all cases, it is most desirable that the dimensions should be correct and consistent for the separate terms in the expression. A formula for wheel-friction attributed to O. Lasche is often quoted, which may be expressed in our units as follows, for a simple wheel with blade-height  $x$ .

$$\text{Wheel-friction} = 0.49 (\text{R.P.M.}/1000)^2 rx/V, \text{ H.P. (O. Lasche.) (23)}$$

This formula seems to give results of the right order of magnitude if we take  $r = 20''$  and  $x = 1''$ , but requires about 370 H.P.

or the wheel of a 10 H.P. De Laval turbine at 20,000 revs./min. at steam at atmospheric pressure, which is about a hundred times so great; and does not distinguish disc- and rim-friction.

Stodola's original formula made the disc-friction proportional to  $r^{3/2}u^3/V$ , and the rim-friction proportional to  $x^{5/4}u^3/V$ , which appears to involve the anomaly that the rim-friction is independent of the radius for given values of  $u$  and  $V$ . Jude (*Theory of the Steam Turbine*, 1910) proposes the formula  $(ux)^{3/2}/V$  for the rim-friction, based on a reduction of the same experiments, in which the disc-friction is assumed proportional to  $r^2u^3/V$ , and the rim-friction deduced by difference. This method of treating the experiments cannot be avoided, but is so uncertain that it appears preferable to make the dimensions rational and consistent by assuming the expression  $rxu^3/V$  as given in (22). So far as rim-friction is concerned, the effective blade-height would be rather less than the actual blade-height, because the ends of the blades are screened by the rim and the shrouding. For this reason  $x$  is preferably taken as the *nozzle-height*, which fits better with the experiments and the expression for the power, and avoids the necessity for the fractional index.

When  $r$  and  $z$  are the same for the different wheels of a turbine, the disc-friction is simply proportional to  $1/V$ , and cannot be altered by varying the arc of admission or the blade-height. A compound wheel has the advantage of reducing the disc-friction, but it increases the rim-friction and the loss due to lateral dissipation of the jet, which is more important and varies roughly as  $1/x$ . In practice the blade-height is varied in conjunction with the arc and angle of admission, to make the sum of the two losses a minimum, with the condition  $\eta x/V \tan \alpha = \text{constant}$ .

To obtain an equivalent formula for the rim-friction of a compound wheel, the numerical coefficient 80 of  $rx$  in (22) must be multiplied by the ratio of the sum of the blade-heights of the successive rings to the height of the first ring. Thus for a triple wheel, if the successive blade-heights are in the ratio 1, 2, 8, the appropriate coefficient of  $rx$  would be  $6 \times 80$ . This appears to give a result of the right order of magnitude, but the conditions of flow and variations of design are so complex that little reliance can be placed on a single formula.

## CHAPTER XII

### THE REACTION TURBINE

**130. Continuous Expansion.** In the case of an impulse turbine, the expansion may be regarded as occurring in a limited number of discontinuous steps, with almost adiabatic drop of pressure in the nozzles, separated by intervals during which the steam changes its state at constant pressure while passing through the blades. The number of separate steps is often as low as five, and seldom exceeds 20 or 30. The final states in each stage will generally lie on a smooth curve, which may be regarded as the "characteristic" of the type of machine, and may be employed for estimating the variation of efficiency. But it is often more satisfactory to calculate each stage separately, and there is no great difficulty in doing this when the number of stages is small.

In a reaction turbine, on the other hand, each ring of blades, whether fixed or moving, constitutes a separate step in the expansion. There are seldom less than a hundred such steps, and sometimes 300 or more. For all practical purposes the expansion is continuous, and different methods of treatment are appropriate. In particular, since the drop of  $H$  or  $P$  in each step is very small, it may usually in practice be treated as infinitesimal. The calculation for a number of stages of similar dimensions, forming a group known as an "expansion," can generally be worked out by the rules of the calculus with a considerable saving of time and trouble. The state of the steam from the beginning to the end of each expansion can be represented by a continuous curve on the diagram. In some cases these separate curves for the several expansions may form parts of a single continuous "characteristic" for the whole turbine. In other cases there may be differences depending on details of construction. But in any case it is usually sufficient to calculate the final state only in each expansion.

In the present chapter we will take the simple case in which the characteristic for the whole turbine is supposed to be continuous, and discuss relations between the efficiency and the pressure distribution which are in the main independent of dimensional details.

At a later stage, the analysis will be pushed further, to include the effect of speed, and dimensions and details of construction, in modifying the curve for each expansion.

**131. The Stage Efficiency.** The expression for the first law of thermodynamics as applied to any elementary stage of the flow, corresponding to a small drop of pressure  $dP$ , may be written in the form

$$dH = dQ + aVdP. \dots\dots\dots(1)$$

According to the usual mathematical convention of signs,  $dH$  and  $dP$  represent *increment* of  $H$  and  $P$ , and  $dQ$  represents heat *added*. But it is often more convenient in practice to reverse the signs and to call  $dH$  *drop* of  $H$ , and  $dP$  *drop* of  $P$ , in which case  $dQ$  represents heat-loss; and heat generated by friction, or work wasted, is negative. The term  $aVdP$  represents the thermal equivalent of the work done by the drop of pressure in generating kinetic energy in unit mass occupying a volume  $V$  as it flows from a higher to a lower pressure. If  $dQ = 0$ ,  $dH = aVdP$ , or the drop of  $H$  is equivalent to the kinetic energy generated; but if heat is supplied by friction or otherwise, the drop of  $H$  will be less than  $aVdP$ . Since friction can only generate heat, the drop of  $H$  cannot exceed the kinetic energy generated unless heat is lost externally. If no heat is supplied or lost *externally*,  $dQ$  represents heat generated by *internal* friction, or work wasted; and  $dH$  represents the useful work obtained. Since external heat-loss may often be neglected in considering any small stage of the expansion, we shall take  $dH$  as representing the work utilised, on the understanding that it is to be corrected for external heat-loss, whenever necessary in experimental tests, by deducting the external heat-loss from the heat-drop.

Neglecting external heat-loss on the above understanding, the general expression for the stage efficiency  $f$  at any point of the expansion curve, is the ratio of the work utilised to the work available in a small drop of pressure  $dP$ ,

$$f = dH/aVdP. \dots\dots\dots(2)$$

If the work done is proportional to the percentage drop of pressure, as appears to be approximately the case in some turbines,  $PdH/dP$  is constant, and  $f$  must vary inversely as  $PV$ . The expansion curve in this case is given by the equation

$$H_0 - H = k \log (P_0/P),$$

and is a straight line on the  $H \log P$  diagram.

In the more general case represented by the empirical formula  $H - B'' = kP^m$ ,

$$afPV = P dH/dP = mkP^{m-1} = m(H - B''), \dots\dots(3)$$

whence  $f = m(H - B'')/aPV$ . This shows that  $f$  cannot be constant unless  $H - B''$  is proportional to  $PV$ , which is very nearly the case for dry steam provided that  $B'' = B = 464$  (F.P.C.), in which case  $f = 18m/8$ . In the case of wet steam  $f$  will also be nearly constant if  $B''$  is chosen so that the ratio of  $PV$  to  $H - B''$  is the same for the initial and final states.

If on the other hand an expansion curve of the type  $PV = kP^m$  is assumed, the value of  $m$  is fixed by the initial and final conditions, and the value of  $f$  at every point of the curve becomes thereby determinate, since there is no other constant to choose. The expression for  $f$  is  $mdH/d(aPV)$ , which is necessarily nearly constant for dry steam, but cannot in general be constant for wet steam. As a rule the variation of  $f$  is so considerable along a curve of this type, that no reliance can be placed on this formula for the calculation of the constant mean value of  $f$  for any given  $F$ . The formula is obviously inadequate for representing the results of experimental tests with regard to the variation of stage efficiency, because the assumption of a curve of this type is equivalent to begging the question at issue.

The exact solution of the problem of the limit curve when  $f$  is constant, is purely a mathematical question if the relation between  $V$  and  $H$  is given. The result is of theoretical interest as a standard of comparison for other empirical curves representing different modes of variation of the efficiency. The problem may also be regarded as a useful mathematical exercise on the tables and equations, and on thermodynamical theory.

### 132. The Limit Curve of Constant $f$ for Dry Steam.

The approximate forms of the equations, obtained by neglecting  $b$ , namely,

$$PV = k'P^{3/13}, \text{ and } H - B = k''P^{3/13}, \dots\dots(4)$$

are sufficiently accurate for nearly all practical purposes.

The exact forms, including  $b$ , are easily obtained by substituting for  $P$  or  $dH/dP$  in the equation  $dH/dP = afV$ , from the general relation between  $H$  and  $V$  for dry steam, namely

$$aPV = 8(H - B)/18 + 10abP/18,$$

which gives differential equations of a common linear type, namely,

$$PdV/dP = \frac{1}{f}(1 - 3f/18)V + 10b/18,$$

$$\text{and} \quad PdH/dP = 3f(H - B)/18 + 10abfP/18, \dots\dots\dots(5)$$

the solutions of which are

$$P(V - b') = k'P^{3/18}, \quad \text{and} \quad H - B = k''P^{3/18} + ab''P, \dots(6)$$

where  $b' = 10b/(18 - 3f)$ ,  $b'' = fb' = 10bf/(18 - 3f)$ , and  $k' = 18ak'/8$ .

The values of the constants  $k'$  and  $k''$  are found in each case as required by substituting the given initial or final values of  $H$ ,  $P$ , and  $V$  in the equations. For instance, the drop of  $H$  along the curve from  $P'$  to  $P''$  is given by

$$H' - H'' = (H' - B' - ab''P')(1 - (P''/P')^{3/18}) + ab''(P' - P''), \quad (7)$$

which reduces exactly to the usual expression for the adiabatic drop, as it should, when  $f = 1$ , in which case  $b'' = b$ .

In the case of supersaturated steam, the same equations apply so long as the steam is dry; but when it reaches the supersaturation limit, the relation between  $H$  and  $V$  changes, and the equation cannot be integrated. It is easy, however, to find the heat-drop at the supersaturation limit by a step by step process of integrating the relation  $dH = faVdP$ , by using Table III given in Chapter X, as in the case of the adiabatic at the supersaturation limit.

Thus if the steam reaches the SS limit at 24 lbs., we have for the next step to 16 lbs.,  $aP'V' = 35.80$ ,  $DH = faPV \times 8/20 = 8.47$ , if  $f = 0.60$ . This gives  $V'' = 20.87$ , and  $aP''V'' = 34.35$ , whence  $DH = 8.468$  as a second approximation; but it is very seldom worth while to go beyond the first. With the value 34.35 for  $aPV$  at 16 lbs., the next step to 12 lbs. gives  $DH = 5.89$ , and so on. The process is very easy, since no interpolation is required, except for finding the point at which the SS limit is reached.

**133. The Limit Curve of Constant  $f$  for Saturated Steam.** To find the equation of the curve for saturated steam, we have merely to substitute  $(H - st)/T$  ( $dp/dT$ ) for  $aV$  in the general expression for  $f$ , which gives the differential equation

$$T(dH/dT) = f(H - st), \dots\dots\dots(8)$$

the solution of which, when  $f$  is constant, is

$$H_f = st + KT'_0 - sT/(1 - f), \dots\dots\dots(9)$$

where  $KT'_0 = H_0 - st_0 + sT_0/(1 - f)$ , is given by the initial state.

The corresponding expression for  $\Phi$ , is immediately obtained by the simple substitution,  $H_1 = T\Phi - G$ , which gives

$$\Phi_1 = KT'^{-1} - s/(1-f) + s \log_e T/273, \dots\dots\dots(10)$$

with the same value of the constant of integration  $K$ . Both expressions take exact account of the variation of specific heat and volume of the liquid according to the equation for  $h$  employed in the present work.

The results given by the above theoretical formula for  $H_1$  are compared in the following table, (1) with those given by a formula of the type  $H - B = kP^m$ , and (2) with those given by a formula of the type  $PV = kP^m$ , with  $F = 0.60$ , for the range 165 lbs. (dry sat.) to 1 lb., divided into ten equal intervals with a common pressure-ratio. The constants in the empirical formulæ are determined from the initial and final states as already explained.

Table I.

Comparison of formulæ for the limit curve of constant  $f$  (saturated).

Theor.	654.49	642.00	630.05	618.61	607.65
(1)	654.55	642.09	630.13	618.66	607.65
Diff.	+ 0.06	+ 0.09	+ 0.08	+ 0.05	+ 0.00
$f_1$	0.553	0.554	0.555	0.556	0.557
(2)	656.26	645.19	634.32	623.62	613.02
Diff.	+ 1.77	+ 3.19	+ 4.27	+ 5.01	+ 5.37
$f_2$	0.480	0.492	0.505	0.519	0.537

Theor.	597.13	587.03	577.32	567.98	559.02
(1)	597.10	586.98	577.27	567.95	559.02
Diff.	- 0.03	- 0.05	- 0.05	- 0.03	0.00
$f_1$	0.556	0.555	0.554	0.553	0.551
(2)	602.43	591.78	581.02	570.12	559.02
Diff.	+ 5.30	+ 4.75	+ 3.70	+ 2.14	0.00
$f_2$	0.559	0.585	0.615	0.648	0.688

Initial values,  $P = 165$ ,  $H = 667.56$ ,  $f_1 = 0.551$ ,  $f_2 = 0.468$ .

There is a slight systematic difference between (1) and the theoretical formula, but the values of  $H$  agree at the middle of the range as well as at both ends. The values of  $f_1$  are very nearly constant, and the mean agrees very closely with the theoretical, which is 0.5551, for  $F = 0.60$  over this range. We may conclude that (1) is sufficiently accurate for all practical purposes. It is also much easier to work than the theoretical formula. In the case of formula (2) the differences are fifty times larger, and the value of



$f_s$  shows a wide variation. The method of calculation for formula (1) is given in detail in Example 8, below, section 138.

**The Reheat Factor.** The ratio of  $F$  to  $f$ , when the latter is constant, is often called the "Reheat Factor," as it represents the increase of  $F$  due to the partial reconversion in the later stages of work wasted in friction in the early stages. Many attempts have been made to find a general expression for this factor in the case of saturated steam. The majority of these are rough approximations which do not call for special mention. Morrow (*Steam Turbine Design*, 1911), under the heading "Approximate Equation of the Expansion Curve," has given an exact expression for the entropy on the assumption that the specific heat of water is constant and equal to 1. His expression agrees very closely with (10) above, but he does not appear to give the corresponding expression for  $H$ , or for  $F/f$ . Martin (*Steam Turbines*, 1913, p. 150) has given a similar expression for the increase of entropy due to friction during the expansion, from which the reheat factor is deduced by integration. His results are in practical agreement with the author's except that he has employed a less simple expression for the entropy of the liquid, which makes a small systematic difference. He takes the range  $T_0 = 820^\circ \text{F.}$  (dry sat.) to  $T = 560^\circ \text{F.}$ , and calculates  $F$  for the following values of  $f$ .

Table II. Comparison of Theoretical values of  $F/f$ .

$f =$	1	0.9	0.8	0.7	0.6	0.5
$F$ (Martin)	1	0.916	0.8286	0.7378	0.6432	0.5455
$F$ (Author)	1	0.9155	0.8279	0.7370	0.6428	0.5451
$F_s$ (§ 134)	1	0.9153	0.8275	0.7367	0.6426	0.5452

The values for the same range according to the author's equation are seen to agree as closely as could be desired. They are obtained from the expression

$$F = (H_0 - H_f) / (H_0 - H_\phi), \dots\dots\dots (11)$$

in which  $H_f$  is the value of  $H$  given by the theoretical formula (9) for the assumed final state and value of  $f$ , and  $H_\phi$  is the final value of  $H$  given by the adiabatic.

The values of  $F_s$  shown in the last line are obtained from a much simpler formula as explained in the next section.

**134. Empirical Formula for the Reheat Factor in the case of Saturated Steam.** The calculation of the value

of  $F$  from the theoretical equation (9) when  $f$  is given, is direct and fairly simple, but the value of  $H_\phi$  is obtained as the difference between two relatively large quantities requiring careful evaluation. The work is even more exacting when  $F$  is given, and it is required to find  $f$ . It is easy, however, to find a simple rational formula, which will serve either purpose with a degree of accuracy exceeding anything required in practice.

The ratio of  $F$  to  $f$  is that of the integral of  $VdP$  along the actual expansion curve, to the same integral taken along the adiabatic. The ratio of corresponding elements of the integrals is obviously  $V_F/V_\phi$ , the ratio of the volumes at corresponding pressures. But in the case of wet steam we have the simple relation

$$V_F/V_\phi = 1 + (H_F - H_\phi)/(H_\phi - st) = 1 + (1 - F) DH_\phi/(H_\phi - st), \quad \dots\dots(12)$$

where  $DH_\phi$  is the whole adiabatic drop to the point considered, and  $FDH_\phi$  is the actual heat-drop by the definition of  $F$ . The differential,  $d(FDH_\phi)$ , of the actual heat-drop is  $afV_F dP$  by the definition of  $f$ . The differential,  $dH_\phi$ , of the adiabatic heat-drop is  $aV_\phi dP$ . We thus obtain the exact relation

$$d(FDH_\phi) = f(V_F/V_\phi) dH_\phi. \quad \dots\dots\dots(13)$$

By substituting for  $V_F/V_\phi$ , integrating, and dividing by  $fDH_\phi$ , we obtain

$$F/f = 1 + (1 - F) DH_\phi/2(H_\phi - st) = 1 + (1 - F)x, \quad \dots(14)$$

where  $x$  is used as a convenient abbreviation for the factor  $DH_\phi/2(H_\phi - st)$ . This expression for the reheat factor would be *exact* if the ratio of  $(1 - F)$  to  $(H_\phi - st)$  were constant along the curve, as assumed in the integration. This condition is so nearly satisfied in all the cases which occur in practice, that the approximation given by the above formula is almost incredibly close, considering its extreme simplicity. The small fraction  $x$ , depending only on  $DH_\phi$  and  $H_\phi$ , is known from the pressure range and initial conditions.  $H_\phi$  is the final value of  $H$  on the adiabatic, obtained by subtracting  $DH_\phi$  from the initial value of  $H$ . The final temperature  $t$  is known from the final pressure.

The ratio  $F/f$  is readily expressed in terms of either  $F$  or  $f$ , thus

$$F/f = 1 + (1 - F)x = 1 + (1 - f)x/(1 + fx), \quad \dots\dots(15)$$

which can be used for calculating either  $F$  or  $f$  if the other is given.

The formula may be verified by comparison with the examples already given. For the case taken in example 1,

$$F = 0.60, DH_{\phi} = 180.89, H_{\phi} - st = 448.06;$$

whence

$$x \pm 0.2019, (1 - F)x = 0.08076, f = 0.5551;$$

which happens to agree exactly with the theoretical value, and was in fact employed in estimating the value of  $f$  to be used in the calculation, in order to make  $F$  come out 0.60. Similarly if we calculate  $F$  from  $f$  for the example taken by Martin, we obtain the values of  $F_x$  shown in the last line of the previous table, which are seen to agree extremely well with the theoretical values over the whole range. The agreement is almost equally good for any other practical range of pressure, and the values obtained are little affected by initial wetness of the steam, as shown in the following examples.

Table III. Empirical Formula for  $F/f$  (sat.).

Pressure range	200 lbs. (dry) to 1 lb.		200 lbs. (dry) to 14.7 lb.		Do. initial 10 % wet	
$f$ (assumed)	0.5	0.75	0.5	0.75	0.5	0.75
$F$ (theoretical)	0.5479	0.7848	0.5274	0.7704	0.5273	0.7702
$F_x$ (empirical)	0.5478	0.7843	0.5271	0.7698	0.5269	0.7696
$F$ (assumed)	0.5	0.75	0.5	0.75	0.5	0.75
$f$ (theoretical)	0.4520	0.7119	0.4728	0.7286	0.4730	0.7288
$f_x$ (calculated)	0.4521	0.7123	0.4730	0.7291	0.4733	0.7293
$f_m$ "	0.4577	0.7162	0.4747	0.7303	0.4749	0.7304

One of the best empirical formulae hitherto proposed for the reheat factor is that employed by Martin in constructing his table of  $F/f$ . He assumes equations of the type  $PV^\gamma = K$ , for both adiabatic and expansion curves, and calculates the appropriate values of the indices  $\gamma'$  and  $\gamma''$  in either case from the pressure-ratio and the expansion-ratios, here denoted by  $\rho$ , and by  $\rho'$ ,  $\rho''$  respectively. This method has the advantage of eliminating most of the systematic error of the  $PV$  type of formula, and gives the symmetrical result

$$F/f_m = \gamma''(\gamma' - 1)(\rho - \rho'')/\gamma'(\gamma'' - 1)(\rho - \rho'), \dots\dots\dots (16)$$

Values given by this formula are indicated by the heading  $f_m$  in the last line of the preceding table for comparison with the values of  $f_x$  calculated by the previous formula for the same values of  $F$  assumed. Martin's formula is inconvenient for calculating  $F$

from  $f_m$  because the final volumes are required. The comparison is accordingly made by calculating  $f_m$  from  $F$ . The values of  $f_m$  obtained deviate from the theoretical in the same direction as those of  $f_w$ , but to a much greater extent; and the calculation of  $f_m$  is much more laborious than that of  $f_w$ , since it involves finding  $\gamma'$  and  $\gamma''$  from  $\log \rho / \log \rho'$ , and  $\log \rho / \log \rho''$ , in addition to finding the volumes from  $H$ , whereas the volumes and expansion ratios are not required for  $f_w$ .

**135. Reheat Factor for Dry Steam.** As might naturally be expected, the value of the factor for dry steam is quite different to that for wet steam. The difference  $F - f$  is about three times as great for dry steam as it is for saturated steam for the same  $f$  and pressure-ratio. This is of special interest in relation to the effect of superheating. If  $b$  is neglected in the equation for dry steam, we obtain as the relation between  $F$  and  $f$ ,

$$F = DH_f / DH_\phi = (1 - (P_f/P_0)^{3/13}) / (1 - (P_f/P_0)^{3/13}) \\ = (1 - (T_f/T_0)^{1/3}) / (1 - T_f/T_0), \dots (17)$$

where  $P_f$ ,  $T_f$ , are the final pressure and temperature on the adiabatic for dry steam. The exact equation for the expansion curve at constant  $f$  is given in a previous section, 132; but the neglect of  $b$  makes very little difference in the present case, and is justifiable as a simplification, because it makes the result depend only on the pressure-ratio  $P_f/P_0$ , which is denoted by  $r$  in the following table.

It is most convenient to tabulate the difference  $F - f$  in place of the ratio  $F/f$ , because the difference is relatively small, and the value of  $F$  when  $f$  is given, or *vice versa*, is more readily obtained by simple addition or subtraction, than by multiplication or division by a factor. The difference is given in the following table for values of  $f$  from 0.9 to 0.45, as shown at the head of each column. The logarithm (base 10) of the pressure-ratio is taken as the argument in the first column, because this gives very regular differences, and greatly facilitates interpolation. The decimal point is omitted in the values of  $F - f$ , which are always positive and less than 1.

When  $f$  is given, the procedure for finding  $F$  is obvious. When  $F$  is given, the value of  $f$  at the head of each column must be added to the tabulated difference  $F - f$ , to find values of  $F$  between which to interpolate. Thus to find  $f$  when  $F = 0.60$ , and  $r = 1/165$ , or  $\log_{10} r = -2.2175$ , we have when  $f = 0.45$ ,  $F = 0.5988$  for  $\log r = -2.2$ , and  $F = 0.6058$  for  $\log r = -2.4$ , whence  $F = 0.5944$  for  $r = 1/165$ .

Similarly when  $f = 0.50$ , we have  $F = 0.6482$  for  $r = 1/165$ . By interpolation when  $F = 0.60$ , we find  $f = 0.4557$  for the given pressure-ratio.

Table IV. Values of  $F - f$  for dry steam.

$\frac{P_f}{P_0}$ $\log_{10} r$	$\frac{DH_\phi}{(H_0 - B) x}$	Values of $f$ .								
		0.9	0.8	0.75	0.7	0.65	0.6	0.55	0.5	0.45
- 0.2	10081	0047	0084	0099	0112	0122	0128	0131	0134	0133
- 0.4	19146	0092	0166	0196	0220	0238	0253	0261	0265	0263
- 0.6	27297	0137	0247	0290	0326	0357	0378	0392	0398	0395
- 0.8	34627	0179	0324	0384	0432	0472	0502	0521	0529	0527
- 1.0	41217	0220	0400	0473	0535	0585	0622	0647	0660	0658
- 1.2	47143	0260	0474	0561	0636	0697	0742	0774	0790	0790
- 1.4	52472	0300	0548	0648	0736	0807	0862	0899	0920	0922
- 1.6	57263	0338	0617	0732	0832	0914	0977	1022	1047	1050
- 1.8	61572	0372	0684	0814	0926	1018	1090	1142	1173	1179
- 2.0	65446	0408	0750	0894	1018	1122	1204	1263	1298	1307
- 2.2	68932	0442	0813	0971	1107	1223	1315	1381	1421	1433
- 2.4	72065	0474	0874	1045	1193	1321	1423	1496	1542	1558
- 2.6	74881	0504	0933	1117	1277	1416	1528	1609	1661	1681
- 2.8	77413	0533	0989	1186	1359	1508	1629	1719	1778	1803
- 3.0	79688	0560	1043	1253	1438	1597	1727	1826	1894	1924

The expression for  $F$ , on which the table is founded, assumes that the *dry* adiabatic is taken as the standard of comparison. When the steam is initially superheated, it may remain dry throughout the whole range of the actual expansion curve, but, for extreme ratios of expansion, the final state on the *adiabatic* will in general be saturated. To find the value of  $f$  from  $F$  for the dry part of the actual expansion curve, the value of  $F$  or  $DH_f$  must be taken from the *dry* adiabatic. If the final value of  $H$ , namely  $H_f$ , is given on the actual expansion curve, and the steam is dry, the calculation of  $f$  for the actual curve can be made without any assumption with regard to the *adiabatic* taken for calculating  $F$ . But if  $H_f$  is not given, and if the given value of  $F$  refers to the *wet* adiabatic, as is usual, the value of  $DH_f$  on the wet adiabatic must be employed for deducing  $H_f$ . In either case the required value of  $f$  is given in terms of  $H_f$  by the formula

$$(P_f/P_0)^{3/13} = (H_f - B)/(H_0 - B),$$

$$\text{or} \quad 1 - r^{3/13} = DH_f/(H_0 - B). \quad \dots\dots\dots(18)$$

For instance, if the value of  $DH_f$  is given as 140 cal. C., and that of  $H_0$  as 756, the value of  $f$  for continuous expansion over the pressure range  $r = 1/165$ , is found to be 0.5541, quite independently

of any assumption with regard to the value of  $F$ . The value of  $f$  is worked out in a similar way in section 143, for this example with ten separate stages, and found to be 0.5686. For given initial and final states the value of  $f$  is a minimum when the number of stages is infinite. The value of  $F$  referred to the wet adiabatic is 0.643, the adiabatic heat-drop being 217.72 cal. C. But the heat-drop along the dry adiabatic to 1 lb. is only 202.20 cal. C., and the value of  $F$  referred to the dry adiabatic is 0.6924. The difference  $F - f$  in the latter case is 0.1885, as found from the above table. The neglect of  $b$  makes a difference of 2 in the last figure. But if the value of  $F$  is taken from the *wet* adiabatic, the difference  $F - f$  is reduced to 0.089. The difference  $F - f$  for steam initially dry and saturated with the same value of  $f$  over the same pressure-range, is only 0.0449. Thus, if we suppose  $f$  to remain the same, superheating will produce a considerable improvement in the relative efficiency.

**136. Effect of Superheating.** In estimating the percentage improvement of  $F$  for the same  $f$ , it is of course necessary to take the *same* adiabatic (either wet or dry) as the standard of comparison for  $F$  in both cases. When the steam is dry for part of the expansion only, this introduces inevitable complications, which reduce the utility of the reheat factor as a method of calculation in such cases. Further complications may be produced by supersaturation, and by the variation of  $f$  in different stages of the expansion. Thus although values of  $F$ , calculated from tables of reheat factors on the assumption that  $f$  is constant, may afford a fair general idea of the nature of the effects to be expected, it is usually safer, and often less troublesome, to calculate the actual heat-drop for the given conditions.

One of the most useful applications of the preceding table in practice is for the calculation of approximate values of the adiabatic heat-drop  $DH_0$  for dry steam, and of the actual heat-drop  $DH_f$ , when  $f$  is given, by means of the formulæ in which  $b$  is neglected, namely,

$$DH_0 = (H_0 - B)(1 - r^{2/13}), \text{ and } DH_f = F(H_0 - B)(1 - r^{2/13}) \dots (19)$$

For this purpose the second column in the table is added giving values (decimal point omitted) of the factor  $1 - r^{2/13}$  by which  $H_0 - B$  must be multiplied to find  $DH_0$ . The table also gives the values of  $F$  required for finding  $DH_f$ , when  $f$  is given.

Thus to find the values when  $H_0 = 756$ ,  $\log r = -2.2$ , and

$f = 0.55$ , we have  $DH_1 = 0.72065 \times 292 = 210.46$ ,  $F = 0.6881$ ,  $DH_1 = 144.82$ .

The calculation is more troublesome when a double interpolation is required for odd values of  $r$  and  $f$ , but the method generally saves time as compared with the use of a table of logarithms. It is most useful for plotting curves, for which purpose even values of  $\log r$  and  $f$  can be selected.

When part of the expansion curve is dry and part wet, the calculation must be made separately for each part. Thus for the dry part of the curve in Example 6, Chapter XIII, with an initial superheat of  $65^\circ \text{C.}$ , we have given the data,  $H_0 - B = 289.84$ ,  $DH_1 = 66.04$ ,  $\log r = -1.10874$ , and we may suppose that it is required to find  $F$  and  $f$  from the table for continuous expansion. By interpolation in column 2 of the table we find

$$1 - r^{3/13} = 0.44439, \quad DH_2 = 106.58, \quad \text{whence } F = 0.6195 \text{ (dry).}$$

From the table, when  $f = 0.55$ ,  $F = 0.6147$  at  $\log r = -1.0$ , and  $F = 0.6274$  at  $\log r = -1.2$ ; whence  $F = 0.6222$  at  $\log r = -1.10874$ . Similarly when  $f = 0.50$ ,  $F = 0.5731$  for the same value of  $r$ . Hence for  $F = 0.6195$ , the required value of  $f$  is  $0.5473$ , to give  $DH_1 = 66.04$  in continuous expansion. For five separate stages the required value is  $0.567$ , as found in § 143 below.

If the value of  $f$  is to be the same for the saturated part of the expansion curve, starting at  $H_0 = 687.80$ ,  $p = 12.845$ , and expanding to 1 lb. we have  $DH_2 = 89.18$ . Taking the formula given in § 184 for  $F/f$  in the case of saturated steam, we find  $x = 0.0874$ ,  $F = f + 0.0250 = 0.5723$ .

The total heat-drop for the whole expansion at  $f = 0.5473$ , is thus found to be  $66.04 + 51.00 = 117.04$ . The adiabatic heat-drop (final state saturated) is  $194.05$ . The overall value of  $F$  is  $0.6080$ . For steam initially saturated at 165 lbs. the value of  $F$  would be  $0.5922$  by the formula of § 184.

When the equation for saturated steam is assumed, the improvement of  $F$  is seen to be relatively small for a moderate degree of superheat ( $65^\circ$ ), as compared with the previous example ( $165^\circ$ ), in which the improvement was  $4\frac{1}{2}$  times as great.

For extreme degrees of superheat, it is evident that the improvement of  $F$  would reach a limit (as referred to the standard adiabatic in which the final state is assumed to be that of saturated steam) when the final state on the adiabatic ceased to be below the saturation limit. Because, when the whole of the adiabatic,

as well as the expansion curve itself, is in the dry region, the relation between  $F$  and  $f$  depends only on the pressure ratio  $r$ , and is practically independent of the temperature.

For the case previously considered with  $r = 1/165$ , and  $f = 0.5541$ , the limiting value of  $F$  would be 0.6924, as found above, for the case in which the adiabatic is dry. The entropy of dry saturated steam at a pressure of 1 lb. being 1.9724, the superheat required in the initial state at 165 lbs. would be far above the limits of Table VI, Appendix III, but is easily calculated from the adiabatic equation  $P/T^{n+1} = K$ , which gives  $T = 1018^\circ \text{C.}$  corresponding to a superheat of  $555^\circ \text{C.}$

It would appear from these examples, in which the usual equation for saturated steam is assumed, that the improvement in  $F$  due to superheat would proceed very slowly at first, then more rapidly, and finally more slowly, reaching a limit at a very high degree of superheat, if  $f$  remains constant. The results of practical tests appear, however, to show that the improvement of  $F$  by superheating is most rapid at first, and is comparatively slow at the practical limit of  $200^\circ \text{C.}$  of superheat. This would indicate that the improvement in the early stages of superheat is largely due to the elimination of losses caused by supersaturation and irreversible condensation, which are not taken into account in the usual theory.

**137. Effect of Supersaturation.** It is possible, by using the reheat factor, to form an estimate of the effect of supersaturation, since it depends chiefly on the properties of the working fluid and little on the mechanism of the engine. For the case of continuous expansion, we may suppose that the expansion proceeds down to the supersaturation limit in the dry state, and that the recovery from supersaturation, which begins at this limit, is also continuous, though both may depend on the rapidity of expansion. Since the point at which condensation begins, as well as the degree of recovery, may vary with the rate of expansion, and since there are no experiments directly bearing on these points, the best that can be done is to calculate a *limit* for the possible effect of supersaturation on the variation of  $F$  with superheat. The simplest available method appears to be that already adopted in a previous section, 107, in calculating the limiting form of the adiabatic for supersaturated steam. In place of the adiabatic relation  $dH = aVdP$ , we have merely to substitute the corresponding relation  $dH = faVdP$



for the limit curve in continuous expansion when  $f$  is constant, employing the relation between  $H$  and  $V$  at the supersaturation limit as defined in the section referred to, in place of the usual relation for saturated steam. The following examples will sufficiently illustrate the method of calculation required.

*Example 1.* Assuming  $f = 0.55$ , and starting with dry saturated steam at 165 lbs. we find from Table IV by the method given for the dry-adiabatic: when  $\log r = -1.0$ ,  $DH_s = 51.58$ ,  $H_s = 615.98$ ,  $P = 16.5$  lbs.,  $H_{ss} = 614.70$ ; when  $\log r = -1.2$ ,  $DH_s = 60.22$ ,  $H_s = 607.84$ ,  $P = 10.41$  lbs.,  $H_{ss} = 611.68$ . By interpolation, the supersaturation limit will be reached on the expansion curve when  $\log r = -1.0455$ ,  $DH_s = 53.90$ ,  $H_s = 613.66$ ,  $P = 14.86$  lbs. The value of  $V$  for dry steam at this point is 22.61 cb. ft. With this value of  $V$ , the heat-drop at  $f = 0.55$  for the next step from 14.86 to 12 lbs. is easily calculated by the formula

$$DH \triangleq 0.55aP'V'(P' - P'')2/(P' + P'') = 4.04, H'' = 609.62.$$

The corresponding value of  $V''$  is 27.66 at the supersaturation limit. The heat-drop for the next step in the table from 12 to 8 lbs. is calculated in the same way with this value of  $V'$ , and found to be 7.51.

Proceeding in this way, we find the whole heat-drop from 165 to 1 lb. at the supersaturation limit to be only 98.0, for  $f = 0.55$ , in place of 107.6 as calculated by the usual formula for saturated steam. In other words the value of  $F$ , referred to the standard adiabatic giving  $DH_s = 180.9$ , is reduced from 0.595 to 0.542, which shows that a reduction of 9 per cent. in the relative efficiency is theoretically possible as the result of supersaturation for steam initially dry and saturated over this range. A reduction of at least 5 or 6 per cent. may reasonably be expected in practice, for moderate rates of expansion under working conditions.

The value  $f = 0.55$ , giving  $F = 0.60$  to 0.69 according to the degree of superheat, is lower than is often attained in many modern machines. If we make a similar calculation with  $f = 0.70$ , giving  $F = 0.787$  to 0.82, we find nearly the same loss of heat-drop over the same range of expansion, representing a somewhat smaller percentage of the whole heat-drop. The mean percentage loss of heat-drop for different values of  $f$ , over the range usual in practice, appears to be nearly 7.8 per cent., which is the same as in the case of the adiabatic drop considered in the previous chapter. Since there is necessarily some uncertainty about the exact form of the

curve representing the supersaturation limit, it will probably suffice in practice to take always the same percentage loss to represent the effect of supersaturation. We therefore propose the following rule.

*Rule.* Find the heat-drop  $DH_f$  for the given value of  $f$  assuming the latter part of the expansion to proceed at the ordinary saturation limit, and deduct 7.8 per cent. of that part of  $DH_f$  which is below the saturation limit in order to represent the effect of supersaturation.

The only difficulty in applying this rule is to find the point at which the expansion curve crosses the saturation line. This can be done with the aid of the preceding table for dry steam by calculating two values of  $DH_f$  and interpolating for the saturation point, for which the nearest even value in Steam Table II, Appendix III, may be taken. Starting from this point we require  $DH_\phi$  for saturated steam in order to find the fraction  $x$  for deducting the required value of  $F$  from  $f_s$ , and to find the loss, which is taken as 7.8 per cent. of  $F \times DH_\phi$ . In the example previously cited, § 186, the heat-drop for the saturated part of the curve is found to be 51.0 cal. C. The loss due to supersaturation, taken at 7.8 per cent., is very nearly 4 cal. C., reducing the whole heat-drop to 113.06 cal. at  $f = 0.547$ , and giving the overall value,  $F = 0.5826$ , with 65° C. initial superheat. By the same rule, with steam initially saturated at 165 lbs., deducting 7.8 per cent. of the corresponding value of  $F$ , namely 0.5922 for saturated steam, we obtain  $F = 0.546$  at the SS limit, showing an improvement of 6.7 per cent. in  $F$  for 65° C. superheat, on the hypothesis of supersaturation, in place of 1.8 per cent. only on the usual theory.

*Example 2.* If the initial superheat is such that the supersaturation limit is not passed, and the steam remains dry, we should naturally expect a considerable reduction in the loss observed. In order to test this point, we may calculate the heat-drop for the case in which the steam just reaches the supersaturation limit,  $H_{ss} = 595.8$ , at a pressure of 1 lb., in which case the initial state  $H_0$  is given by the condition,  $H_0 - DH_f = 595.8$ . But from Table IV, for  $\log r = 2.2175$ , with  $f = 0.55$ ,  $F = 0.689$ , we find

$$DH_f = (H_0 - B) \times 0.477.$$

Whence  $H_0 = 715.9$ , and  $DH_f = 120.1$ . This gives  $t_0 = 272.5$  or an initial superheat of 87° C., with  $\Phi_0 = 1.6657$ . With the usual equations for saturated steam the adiabatic heat-drop is 199.1,

and the actual drop for  $f = 0.55$  is 121.9. The corresponding values of  $F$  are, 0.612 for saturated, and 0.608 for dry supersaturated steam, showing a great reduction in the loss due to supersaturation for a moderate degree of superheat.

By calculating a few more values in this way for various degrees of superheat, with  $f = 0.55$ , the curves shown in the annexed Fig. 80 are obtained. The curve marked S shows the variation of  $F$  with superheat when  $f$  is constant, in very slow expansion, when the steam has time to follow the ordinary saturation state. The curve marked SS shows the same variation for the case in which the expansion is so rapid that no condensation occurs until the supersaturation limit is reached, and the steam remains at the super-

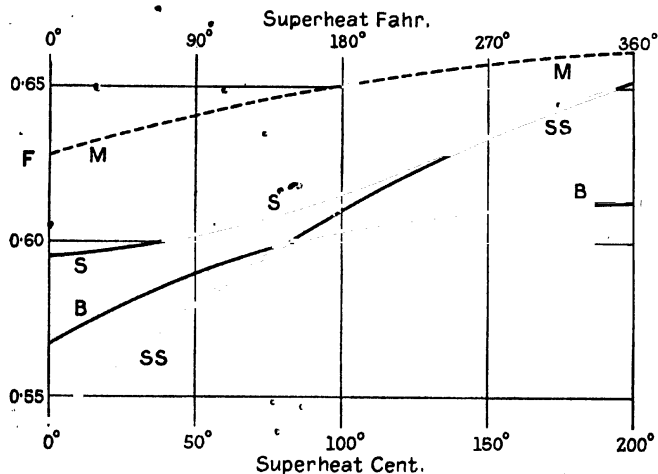


Fig. 30. Effect of Supersaturation on the variation of  $F$ .

saturation limit for the rest of the expansion. In the present example, the two curves meet at a superheat of  $165^{\circ}\text{C}$ ., sufficient to keep the steam superheated throughout the whole expansion curve, so that supersaturation is no longer possible. But the limit of the theoretical improvement of  $F$  due to superheat is not reached until  $F = 0.689$  at a superheat of  $555^{\circ}\text{C}$ .

The curve marked B is that given by Baumann (*Journ. Inst. Elect. Eng.*, No. 218, vol. 48, p. 828, 1912), as the result of a number of tests on impulse turbines. It shows a rate of improvement intermediate between S and SS, for moderate degrees of superheat. It might naturally be supposed that the rate of expansion in an

actual turbine was not sufficiently rapid to keep the steam at the SS limit. The loss due to supersaturation would, then, be less than the limit above calculated, and the improvement due to superheat also less, though greater than could be accounted for on the usual theory of saturation. There is also the objection to the reheat method that the reheat factor is appreciably less for discontinuous expansion in an impulse turbine than for continuous expansion as here assumed, and that the stage-efficiency  $f$  cannot be constant throughout the expansion in any given machine. These objections to the use of the reheat factor in calculating the improvement due to superheat are not without weight, and appear at first sight to explain the discrepancy between the curves B and SS to a certain extent, in a qualitative manner; but when examined quantitatively they are found to be quite inadequate, especially in the region of high superheat, where the effect of supersaturation is practically non-existent.

There is, however, a much more important difference between the conditions assumed in calculating the curve SS and those applying to the experimental curve B, which is capable of explaining the whole discrepancy and tends to show that the steam must remain very near the SS limit at the actual rate of expansion corresponding to curve B. In calculating the curve SS, it was tacitly assumed that the stage-efficiency  $f$  remained constant when the conditions were changed. This could not happen in practice unless the dimensions or the speed of the machine were altered to suit the change of conditions, which would usually be impracticable. The curve B illustrates the actual change of  $F$  for a *given* machine, designed for  $150^{\circ}$  F. superheat, when the superheat is varied without making any modifications in the design or the speed. It is evident that if a machine designed for  $150^{\circ}$  superheat is run at  $300^{\circ}$  F. superheat, it will not give the best results obtainable at the higher superheat. An exact calculation of the effect for a given machine requires a knowledge of the dimensions and pressure distribution, as explained in a later chapter; but the calculation here made with the aid of the reheat factor, assuming  $f$  constant, affords a very fair qualitative estimate of the effect of supersaturation and the advantage to be gained by superheating, if the dimensions are suitably modified.

The dotted curve marked M in the upper part of the figure represents the improvement of  $F$  calculated for a *particular turbine* of given dimensions, when the superheat is varied from  $0^{\circ}$  to  $200^{\circ}$  C.

without change of speed, or pressure-range, or dimensions. This curve is calculated by a method explained in a later section, in which allowance is made for the variation of the stage-efficiency with superheat. The average value of  $f$  for this case is somewhere in the neighbourhood of 0.60 in place of 0.55, but  $f$  necessarily diminishes with superheat when the dimensions remain constant. It will be seen that curve M corresponds very closely with Baumann's experimental results in the region of high superheat, but shows a somewhat smaller improvement for moderate degrees of superheat. If the calculation were made for the same machine on the assumption that the dimensions were modified to suit the superheat in such a way as to keep  $f$  constant (though not necessarily constant throughout the turbine at any given superheat), it would show a much greater improvement with superheat, approximating more nearly with that shown by the curve SS. The great difference which exists between the two cases, M and SS, or B and SS, illustrates the importance of designing a turbine to suit the degree of superheat at which it is intended to work, if it is desired to obtain the full theoretical advantage of the superheat. It should also be remarked that if allowance had not been made for the effects of supersaturation in calculating the curve M, the result would have shown an appreciable *diminution* of  $F$  with superheat, which is quite contrary to experience. The fact that curve M shows a slightly smaller improvement than curve B for moderate degrees of superheat may be due to reduction of friction, which would affect curve B, but of which no account has been taken in the calculation of curve M. It appears that wheel friction is greater in wet than in dry steam under similar conditions (Stodola, *The Steam Turbine*, p. 137), and diminishes with the density. But the diminution of friction does not seem to be sufficient to account for the whole of the improvement observed.

### 138. The Condition of Equal Work per Expansion.

A condition commonly assumed in design is that of equal division of work between the stages or expansions. Such a condition is mechanically appropriate, and has the advantage of simplifying the calculation, if a formula of the type  $H - B = kP^n$  is employed, because the successive values of  $H - B$  can be written down by equal differences, and afford the simplest possible method of calculating  $p$  and  $V$ . If  $f$  is assumed to be constant, the calculation is very simple, but the formula may also readily be applied to

represent any desired range of variation of  $f$  in a continuous manner. In the majority of cases the formula affords a much more expeditious and accurate solution than can be obtained from any diagram, because, except in special cases, the expansion curve is difficult to draw on the diagram, and the required measurements on the curve when drawn do not admit of the same degree of accuracy as the calculation.

The method of applying the formula under these conditions to the case of a reaction turbine is illustrated by the following examples.

*Example 8.* In the case of a reaction turbine with ten expansions, if  $f$  is constant, and  $F = 0.60$ , find the pressures required at the nine intermediate points to give equal division of work between the ten expansions, and calculate the corresponding values of the volume, taking the range 165 lbs. (dry sat.) to 1 lb.

The order of the calculation is as follows:

(1) Find  $DH_\phi = 180.89$ , and  $H_\phi'' - st'' = 448.06$ , from the Tables.

(2) Find  $f$  from  $F/f = 1 + (1 - F)x$ . Here  $x = 0.2019$ , and  $f = 0.5551$ .

(3) Find  $H' - H'' = 108.58$ , and  $H'' = 559.02$ , from  $F = 0.60$ .

(4) Find  $V' = 2.7801$  from the Tables, and deduce  $V'' = 302.08$  from  $H''$ .

The above operations cannot be avoided in any method of calculation. The application of the empirical formula for intermediate points is as follows:

(5) Find  $H'' - B'' = p''V'''(H' - H'')/(p'V' - p''V'') = 209.81$ .  
 $H' - B'' = 317.84$ .

(6) Add 10.858 nine times in succession to  $H'' - B''$ , giving the values of  $H - B''$  at the nine intermediate points required. These are shown in the first line of the following table under the corresponding point numbers. The initial and final values already given are omitted to save space. Similarly for any desired number of expansions  $N$ , the common difference is  $(H' - H'')/N$ .

(7) Take the logs of  $H - B''$  as shown in the next line. The characteristic of the logarithm, and the decimal point, are omitted in each case, since the characteristic is always 2, and is not required in the calculation.

(8) Subtract  $\log(H'' - B'') = 2.82080$ , from each, giving the values in the next line.

(9) Find  $\log(p'/p'') = 2.2175$ , and reduce all the logs in the

ratio  $1/m$ , where  $m = 0.18141/2.2175 = 0.08180$ , being the ratio of  $\log(H' - B'')/(H'' - B'')$ , already found, to  $\log(p'/p'')$ . This gives the logs of the  $p$  ratios in the next line. Since the ratio  $1/m$  is constant, the operation of reduction is very easily performed, preferably with a Fuller slide-rule, which gives ample accuracy for the purpose.

(10) Add  $\log p''$  (in this case 0) to each of the values of  $\log(p/p'')$ . Take the antilogs giving the required values of  $p$  shown in the next line.

(11) Approximate values of  $V$ , sufficiently accurate for almost any purpose, are most easily found from those of  $p$  and  $H - B''$  by the simple formula

$$V = m(H - B'')/afp, \dots\dots\dots(20)$$

since  $m/af = 0.08180 \times 1400/144 \times 0.5551 = 1.4380$ , is a constant factor in the present instance. The values so obtained are given in the next line, headed  $V$  (approx.), and are more accurate than any which could be found from a diagram, in addition to being more easily obtained. By way of verification the correct values of  $V$  for each  $H$  and  $p$  have been calculated from the tables by the exact formula, and are shown in the next line headed  $V$  (correct). But the exact method for  $V$  is far more troublesome than the approximate formula (20), owing to the necessity of interpolation for  $H$ , and  $V$ , and  $t$  at each point, and should be employed only if  $V$  is required for small differences, which is very seldom the case, unless it is necessary to calculate  $H$  from  $V$ , as in employing a formula of the type  $PV = kP^m$ .

Table V. Results for Example 3.  $f = 0.555$  (constant),  $B'' = 850$ .

Point No.	1	2	3	4	5	6	7	8	9
$(H - B'')$	306.09	296.13	285.28	274.43	263.58	252.72	241.87	231.02	220.1
$\log(H - B'')$	48712	47149	45527	42843	42090	40264	38358	36364	3427
$\log(H - B'')$	16632	15069	13447	11763	10010	08184	06278	04284	0219
$\log(p/p'')$	2.0332	1.8422	1.6440	1.4380	1.2237	1.0004	0.7674	0.5238	0.268
$p$ lbs.	107.94	69.535	44.056	27.416	16.738	10.001	5.8533	3.3404	1.854
$V$ (approx.)	4.075	6.102	9.278	14.34	22.57	36.22	59.21	99.10	1701
$V$ (correct)	4.094	6.113	9.278	14.32	22.52	36.11	59.06	99.10	1704

The point of the foregoing method is that all the arithmetical operations are very simple and easily performed, and that the results possess nearly as high an order of accuracy as could be obtained by the most exact theoretical equations, involving a

prohibitive amount of labour. A similar solution is obtained with almost equal ease for any desired range of variation of  $f$ , a problem which would be otherwise insoluble except by a very laborious method of trial and error. The simplest method when  $f$  is variable is illustrated in the following example.

*Example 4.* With the same initial and final data as in the preceding example, find the pressures and volumes at nine intermediate points, required for equal work in each of ten expansions, and calculate the values of the stage efficiency at the intermediate points, if the ratio  $f'/f''$  of the initial and final values of  $f$  is  $5/6$ .

The work is the same as in the previous example with the exception of the determination of  $H'' - B''$ , and the intermediate values of  $f$  and  $V$ .  $H'' - B''$  is found from the condition  $f'/f'' = 5/6$  combined with the general expression for  $f$  which gives

$$f' = m (H' - B')/ap'V', \quad f'' = m (H'' - B'')/ap''V'',$$

whence

$$H'' - B'' = 6p''V''(H' - H'')/(5p'V' - 6p''V'') = 408.99,$$

$$H' - B'' = 517.52.$$

The required values of  $H - B''$  are given in the first line of the following table. Those of  $p$  are obtained, exactly as in the previous case, by logarithmic interpolation. The values of  $pV$  given in the next line are obtained in the same way by reducing the logs of  $(H - B'')/(H'' - B'')$  in the ratio of  $\log(p'V'/p''V'')$  to

$$\log (H' - B'')/(H'' - B'').$$

These are required for finding the intermediate values of  $f$  and  $V$ , and are sufficiently accurate for this purpose, though not so accurate as the values of  $p$ . The correct values of  $V$  deduced from  $H$  are given in the last line for comparison.

Table VI. Results for Example 4.  $f' = 0.506$ ,  $f'' = 0.607$ ,  $B'' = 150.0$ .

Point No.	1	2	3	4	5	6	7	8	9
$- B''$	506.67	495.81	484.96	474.11	463.26	452.40	441.55	430.70	419.84
bs.	104.24	65.17	40.34	24.67	14.93	8.921	5.270	3.071	1.765
	441.8	425.1	408.7	392.7	376.9	361.3	346.1	331.1	316.4
	0.514	0.523	0.532	0.541	0.551	0.561	0.572	0.583	0.595
approx.	4.238	6.523	10.13	15.92	25.24	40.49	65.67	107.8	179.3
(correct)	4.233	6.507	10.10	15.84	25.10	40.29	65.33	107.4	178.9

The maximum error of  $V$  by the approximate method of calculation is only  $1/2$  of 1 per cent. The change in the assumption



for  $f$  makes a difference of 12 per cent. in the values of  $p$  and  $V$  at stage 5, for the same value of  $H$  in both cases.

As further examples of the equal division of work in continuous expansion, we may take two simple cases in which the characteristic curves are readily drawn on the diagram, so that the solution may also be obtained graphically.

*Example 5.* The simplest case is that represented by the equation  $H - B'' = k \log p$ , in which equal pressure-ratios give equal division of work, corresponding to a straight line joining the initial and final states on the  $H \log P$  diagram. The constant  $B''$  is the value of  $H$  when  $p = 1$ , and the constant  $k = (H' - H'')/\log(p'/p'')$ . The efficiency at any point in continuous expansion is  $f = 0.4848k/apV$ . The following table shows the values of  $p$ ,  $V$ , and  $f$ , at nine intermediate points of the expansion from 165 lbs. to 1 lb. The values of  $p$  and  $V$  are the same as in Example 2 of the next chapter, but those of  $f$  differ slightly from those given in the example cited, in the case of saturated steam, because they are the values at each point in place of being the mean values over the preceding stage. The values of  $V$  (approx.), calculated as a geometrical progression, agree sufficiently closely for practical purposes with those of  $V$  (correct) calculated from  $H$ .

Table VII.

$$H - B'' = k \log p, \quad H' - B'' = 559.02, \quad f' = 0.450, \quad f'' = 0.684, \\ k = 48.94.$$

Point No.	1	2	3	4	5	6	7	8	9
$H$	656.71	645.85	635.00	624.14	613.29	602.43	591.58	580.73	569.87
$p$	99.02	59.43	35.66	21.40	12.84	7.710	4.626	2.777	1.666
$V$ (correct)	4.447	7.111	11.37	18.17	29.02	46.36	74.02	118.4	189.2
$V$ (approx.)	4.443	7.100	11.35	18.13	28.98	46.31	74.01	118.3	189.0
$f$	0.470	0.490	0.510	0.532	0.555	0.579	0.603	0.629	0.656

*Example 6.* The characteristic curve obtained when  $F$  is assumed constant, is also easily drawn on the diagram by reducing the ordinates of the adiabatic in the constant ratio  $F/1$ . This is represented for the case  $F = 0.60$  by the curve AFC joining the points AC on the diagram, Fig. 82. The pressures corresponding to equal division of work are found by drawing horizontal lines to meet the curve AFC at equal differences of  $H$ . The volumes can then be read from the diagram, and the values of  $f$  deduced from the slope of the curve at each point. But it is just as easy to perform the same

operation by calculation in the following manner, with the aid of the empirical formula  $H - B' = k'p^{1/9}$  for the adiabatic IX (29), and a similar formula  $H - B'' = k''p^m$  for the expansion curve. Since  $F$  is to be constant, we must have  $m = 1/9$ , and  $k''/k' = F$ . The logarithm of the ratio of the initial and final values of  $H - B''$  is  $(1/9) \log (p'/p'')$ . Taking  $F = 0.60$ , for the range 165 to 1 lb., we find  $(H' - B'')/(H'' - B'') = 1.76855$ , or

$$H'' - B'' = 108.53/0.76855 = 142.14.$$

The values of  $H - B''$  for equal division of work at nine intermediate points are obtained by successive addition of 10.853 to  $H'' - B''$ . The required values of the pressure are then obtained by logarithmic interpolation as previously explained. The values of  $V$  may be deduced from those of  $H$  and  $t$  if great accuracy is required, but for most purposes it suffices to find the intermediate values of  $pV$  by logarithmic interpolation from the initial and final values as previously explained. The values of  $f$  are obtained from the formula  $f = m(H - B'')/apV = 1.080(H - B'')/pV$ . The values of  $f$  and  $V$  deduced from the approximate values of  $pV$  will be in error by about 1 per cent. at point 5 in the present case, but since the effect of supersaturation may amount to 5 per cent. or more, an error of 1 per cent. in  $V$  would not be serious in practice in comparison with the uncertainty of supersaturation, and with the large differences in both  $p$  and  $V$  occasioned by making different assumptions for the variation of  $f$ .

Table VIII.  $F = 0.60$  (const.),  $H'' - B'' = 142.14$ ,  $m = 1/9$ ,  
 $f' = 0.590$ ,  $f'' = 0.508$ .

Point No.	1	2	3	4	5	6	7*	8	9
$H - B''$	239.82	228.96	218.11	207.26	196.40	185.55	174.70	163.85	152.99
$p$	110.8	73.02	47.17	29.80	18.36	11.01	6.400	3.593	1.938
$pV$ (approx.)	444.0	429.1	414.0	398.8	383.3	367.6	351.6	335.4	318.8
$V$ (approx.)	4.008	5.876	8.776	13.38	20.88	33.39	54.93	93.34	164.4
$f$	0.583	0.576	0.569	0.561	0.554	0.545	0.537	0.528	0.518

Comparing Examples 5 and 6, we observe that the value of the pressure at point 5, namely 18.36 on the assumption  $F$  constant in Example 6, exceeds that found at the same point in Example 5, namely 12.84, by 43 per cent. These two cases represent two of the assumptions most commonly made for the expansion curve, and

illustrate the practical importance of a more complete experimental investigation of the question than has yet been attempted.

### 139. Graphic Comparison of Characteristic Curves.

The characteristic curve of a turbine represented by the differential equation  $dH = cfVdP$ , may be defined as the relation between  $H$  and  $P$  (or preferably between  $H$  and  $\log P$ ) resulting from the variation of the stage efficiency throughout the expansion. It is evident from the form of this relation that the  $H \log P$  diagram is the most appropriate for the exhibition of such curves over an extended range of pressure. Examples of such curves drawn on the diagram are exhibited in Fig. 32. When the form of the curve representing the performance of any particular type of machine is known, the required calculations are greatly facilitated, especially

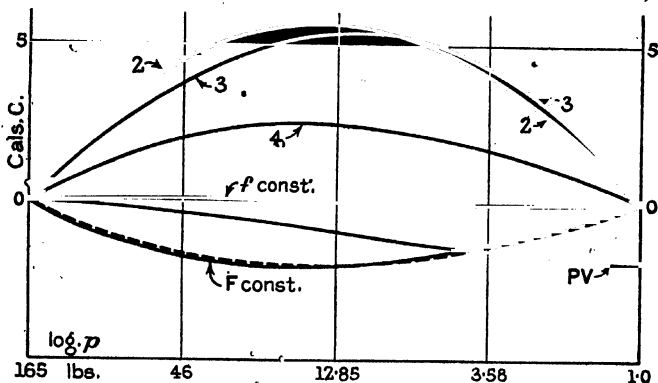


Fig. 31. Differences between types of Characteristic Curves.

in the case where the stages are numerous. When the variation of  $f$  is continuous, it appears from the foregoing examples that the curve may most conveniently be represented by an empirical formula of the type  $H - B = kP^m$ , which covers a wide range of possible varieties, and is very convenient for computation.

The annexed Fig. 81 is intended to give some idea of the differences between different cases for saturated steam, and to show how closely they can be represented by the empirical formula. The range of expansion is from 165 lbs. (dry sat.) to 1 lb., and the case in which  $f$  is constant is taken as the standard of comparison, represented by the horizontal base line. The ordinates of the curves represent differences from this standard in cal. C. The scale of

pressure along the base line is logarithmic. The initial and final states are the same on each curve, and correspond to  $F = 0.60$ , or a total heat-drop of 108.58 cal. C. The curve coinciding most closely with the base-line is the empirical formula (1) of Table I, showing deviations of less than 0.05 cal. on the average from the theoretical curve. The curve marked 3 represents the formula  $PV = kP^m$ , which shows deviations of 5 per cent. from the curve of constant  $f$ , and gives a range of variation of  $f$  in the ratio  $f'/f'' = 5/7$  nearly. This curve appears to represent with a fair degree of approximation the actual performance of some reaction turbines, and coincides very closely with the curve marked 2, representing the empirical formula  $H - B = k \log P$  of Example 5, which gives a straight line on the  $H \log P$  diagram. The latter formula is a special case of the general type  $H - B = kP^m$ , which reduces to the logarithmic form when  $m = 0$ . The curves represented by the general formula, when drawn on the  $H \log P$  diagram, have the same kind of curvature as the adiabatic for positive values of  $m$ , but the opposite curvature when  $m$  is negative. It is probable that curves with negative values of  $m$  may represent the case of small turbines in which the efficiency is very low in the early stages. The curve 4 represents the intermediate case of Example 4 in which the range of variation of  $f$  is represented by the ratio  $f'/f'' = 5/6$ . The lowest curve in the figure is the curve of constant relative efficiency  $F$ , which is of interest because it is often assumed on account of its simplicity, being represented by a straight line on the Mollier diagram. It lies below the theoretical curve of constant  $f$ , as shown in the figure, and would make  $f$  diminish continuously throughout the expansion (giving a range of variation represented approximately by the ratio  $f'/f'' = 7/6$ ) which is highly improbable. The dotted curve representing the formula  $H - B'' = kp^{1/3}$ , of Example 6, is seen to agree very closely with the theoretical curve of constant  $F$ .

The curve marked  $PV$  shows the result obtained by calculating the heat-drop at intermediate points from the expression

$$af_m(p'V' - p''V'')/m$$

for the integral of  $af_m V dp$  along the curve  $pV = kp^m$ , in which the value of  $f_m$  is taken as constant, and is deduced from  $F$  by the formula for the reheat-factor given by Martin. This is fairly accurate in the early stages, but has the disadvantage of leading to a discrepancy of 1.6 per cent. in the final state. The method applies only to the case  $f$  constant, and is more troublesome than that of Example 3, in addition to being less accurate.

The above examples refer to the case of *saturated* steam, and show that an empirical formula of the type  $H - B'' = kp^m$  possesses the required degree of flexibility and accuracy for practical purposes. It is equally appropriate in the case of superheated or supersaturated steam, because it fits more naturally with the theoretical equations than in the case of saturated steam. On the other hand a formula of the type  $PV = kP^n$ , though so commonly employed for the same purpose, possesses no flexibility, and can only represent one particular type of expansion curve, which may or may not correspond with experiment.

If the characteristic curve is known for a particular type of machine, the diagram is useful for estimating the volume and heat-drop at intermediate points of the expansion by observing the corresponding pressures. Changes in the state of the steam, or accidental defects of efficiency, may thus be detected. Unfortunately the published data for intermediate pressures are so scarce and unreliable that it is difficult to find satisfactory examples of actual cases. But if the dimensions are known, and accurate observations of pressure are obtainable, better results may be deduced by calculation, as illustrated in Chapter XVI, because the form of the characteristic curve may vary with changes of state of the steam and other conditions, and can seldom be predicted in minor details.

## CHAPTER XIII

### THE IMPULSE TURBINE

**140. Subdivision of the Heat-Drop for a Multistage Impulse Turbine.** The method usually adopted in theoretical works in conjunction with the entropy diagram, is to divide the adiabatic heat-drop, or the area on the  $T\Phi$  diagram, or the  $PV$  diagram, representing the whole available energy, into a number of equal parts, assuming that the efficiency is constant throughout the expansion. A method more commonly adopted in practical design is to assume equal pressure- or expansion-ratios for the different stages, which simplifies the calculation. In either case it is important to maintain a suitable ratio between steam- and blade-velocity, and the subdivision of the heat-drop must be modified if there is any considerable difference between the stages, such as would be occasioned by the use of compound wheels, or of simple wheels of different diameters.

The most uncertain element in the calculation is the final state of the steam in each stage, or the residual supersaturation, which depends on the rapidity of expansion, and on the leakage and frictional losses occurring in each stage. There is little direct experimental evidence on the variation of the efficiency from stage to stage, though it is generally admitted that the efficiency must be lower in the early than in the later stages, for reasons already discussed. This difficulty is evaded in most of the following examples, by assuming a particular type of expansion curve and finding the resulting efficiencies, or by assuming the efficiencies themselves, in which case the result would be definite apart from the phenomena of supersaturation.

In dealing with the effects of supersaturation, it is always possible to calculate upper and lower limits for the effect. For this reason many of the calculations are made for steam in the equilibrium state of saturation, giving the upper limit, as well as for supersaturated steam at the lower limit, and for certain combinations of these assumptions which appear to be possible or instructive. Further light on this important question can be obtained only

by comparison of calculations of this nature with the results of experimental tests. There are few satisfactory data available at present, but these seem to show that steam in rapid expansion keeps very close to the supersaturation limit.

Since the variation of relative efficiency from stage to stage remains as a subject for experiment, and is probably different for different types of machine, it is impossible to give definite rules applicable to all cases for the subdivision of the pressure-range or heat-drop. The following examples are intended merely to illustrate the methods of using the tables in calculating the required quantities, and to show the effect of different assumptions for the variation of the efficiency. To facilitate comparison, the same pressure-range, namely 165 to 1 lb., starting with dry saturated steam, is assumed in the first series of examples, and the range is divided into ten parts in each case, so as to give an approximately equal division of work between the stages. In order to simplify the calculation it will be assumed in the first instance, (1) that the expansion in each nozzle is adiabatic and frictionless, (2) that after passing through the blades, and before expanding through the next nozzle, the steam is reduced to the equilibrium state of saturation corresponding to the actual heat-drop deduced from the assumption made with regard to the efficiency in each case. The velocities and nozzle areas calculated on these assumptions may require correction for friction in the nozzles and will be affected materially by supersaturation lag. But the above method of calculation represents a definite limit corresponding closely with the conditions generally assumed.

The notation adopted for the different stages is as follows. The suffix  $_0$  is used to denote the initial condition of the steam at  $P_0H_0$  before expansion through the first nozzle, assuming  $U = 0$ . Suffices 1, 2, 3, etc. refer to the consecutive stages of the expansion at pressures  $P_1, P_2$ , etc. in the wheel chambers. The initial state in each chamber on leaving the nozzle is indicated by a single dash, the final state before entering the next nozzle, by a double dash. Thus  $H_0 - H_1'$  represents the adiabatic heat-drop in the first nozzle,  $H_3'' - H_4'$  that in the fourth nozzle. The adiabatic heat-drop in any nozzle may also be represented by the convenient abbreviation  $DH_\phi$ . Similarly,  $DH_1''$  represents the actual heat-drop in the first stage, and  $DH_4''$  that in the fourth stage. The symbol  $H_\phi$  is employed to denote the value of  $H$  on the adiabatic through the initial state at a point corresponding to the pressure in each

chamber. The drop of temperature, pressure, or potential per stage may similarly be represented by the abbreviations,  $Dt$ ,  $Dp$ ,  $DG$ .

*Example 1.* Find the temperatures along the adiabatic for saturated steam, corresponding to the subdivision of the adiabatic heat-drop from 165 lbs. (dry saturated) to 1 lb. into ten equal parts. If the relative efficiency  $F$  is constant and equal to 0.60 throughout the expansion, find the actual efficiency  $f$  of each stage, and deduce the velocities and nozzle-areas.

The whole adiabatic heat-drop in this case is 180.88 as previously calculated, and the values of  $H_\phi$  corresponding to the temperatures in each stage are obtained by successive subtraction of 18.088 (a tenth of the total heat-drop) from the initial value, namely,  $H_0 = 667.56$ . These values are given in the second line of the table below, under the numbers of the corresponding stages. The required temperatures are most easily found from the adiabatic equation,  $T\Phi_0 = H_\phi + G$ , since  $H_\phi$  and  $\Phi_0$  are given, and  $G$  is a function of  $T$  only, tabulated for each  $1^\circ \text{C}$ . Thus for the first stage, substituting the initial values of  $H$  and  $\Phi$ , we obtain as the equation for  $t$ ,  $t = 140.82 + G/1.5691$ , which is easily solved by interpolation. Thus taking  $t = 168^\circ$ ,  $G = 43.33$ , we find  $t = 168.48^\circ$ , and taking  $t = 169^\circ$ ,  $G = 43.81$ , we find  $t = 168.74^\circ$ . By interpolation,  $t = 168.62^\circ$  is the solution. Proceeding in this way we obtain the values of  $t$  given in line 3, from which the corresponding values of  $p$ ,  $H_s$ , and  $V_s$ , are readily found by interpolation in the Steam Tables II or III, App. III. The values of the constant in the equation for  $t$  in successive stages are obtained by successive subtraction of  $18.088/1.5691 = 11.528$  from 140.82. The required values of  $t$  may be obtained from the tables in many other ways, but the above method is probably the simplest and most accurate. It is far preferable in point of simplicity and accuracy to the division of the area on the entropy diagram into equal parts, which is so commonly recommended as a method of solving this problem.

In order to find the values of the actual adiabatic drop  $DH_\phi$  in each nozzle, we require the values of  $H''$  at the end of each stage. These are readily found from the condition that  $F$  is constant and equal to 0.60, by subtracting the constant difference

$$18.088 \times 0.60 = 10.853$$

for each stage. The adiabatic drop  $DH_\phi$  might then be found from the usual formula  $DH_\phi = \Phi''Dt - DG$ , where  $Dt$  is the temperature drop for the nozzle considered, by deducing  $\Phi''$  from  $H''$  in each



case. But since we already have the relation  $18.088 = \Phi_0 Dt - DG$ , we find

$$DH_\phi = 18.088 + (\Phi'' - \Phi_0) Dt = 18.088 + (H' - H_\phi) Dt/T. \dots (1)$$

For the first nozzle  $H'' = H_0$ , and  $DH_\phi = 18.088$ . For the second nozzle, we have  $H'' - H_\phi = 7.24$  from column 1,  $Dt = 16.81$  from 1 and 2, and  $T = 441.72$  from 1, which gives 0.267 to be added to 18.088 for the adiabatic heat-drop. It is advantageous to work the solution in this way, because the point of the problem is to investigate the manner in which the actual heat-drop  $DH_\phi$  in each nozzle deviates from the constant value 18.088 assumed in the division of the heat-drop along the adiabatic. The correction term is so small that it can easily be worked on a small slide-rule with little chance of error in the second decimal place, even if the values of  $Dt$  are not quite accurate.

The stage efficiency  $f$ , given in the next line, is found by dividing the constant difference  $DH'' = 0.60 \times 18.088 = 10.853$  by the value of  $DH_\phi$  for the nozzle considered. It will be seen that the value of  $f$  diminishes considerably in the later stages as compared with the earlier. Since in all turbines the later stages are the most efficient, we infer that the assumption of constant relative efficiency  $F$  throughout the expansion cannot be correct, and that there is no advantage, even in simplicity of calculation, to be derived from the equal division of the adiabatic heat-drop which is so often recommended.

The values of the initial velocity  $U'$  in feet per second given in the next line are obtained by multiplying the square root of  $DH_\phi$  by the constant 800.2. They show a nearly uniform rate of increase from stage to stage. Since the velocity carried over from stage to stage also tends to increase in the later stages, the realisation of the condition  $F = \text{constant}$  would require a very marked reduction in the wheel efficiency at low pressures, which is quite contrary to experience.

The initial value of  $H'$  in each stage is obtained by subtracting  $DH_\phi$  from the final value of  $H''$  in the preceding stage. The values of  $V'$  at the exit from each nozzle are deduced from those of  $H'$  by the formula for saturated steam, with the aid of  $H_s$ ,  $V_s$ , and  $s$  in the usual way. The appropriate nozzle areas per pound follow from the relation  $X'/M = 144V'/U'$ . The pressures given in the last line are not required in the calculation, but are useful for purposes of comparison. Thus, in testing a turbine constructed on

these lines, it would probably be found that the observed pressures did not correspond with the calculation in consequence of the erroneous assumption made with regard to the relative efficiency.

Table I. Results for Example 1. F.P.C. units.

No.	1	2	3	4	5	6	7	8	9	10
$P_0$	649.47	631.38	631.29	595.21	577.12	559.03	540.94	522.85	504.77	486.68
	168.62	152.31	136.54	121.25	106.44	92.10	78.16	64.64	51.50	38.74
$P''$	656.71	645.85	635.00	624.15	613.30	602.44	591.59	580.74	569.88	559.03
$H_0$	18.088	18.355	18.643	18.924	19.211	19.500	19.794	20.097	20.406	20.722
	0.600	0.591	0.582	0.574	0.565	0.556	0.548	0.540	0.532	0.524
$V'$	1277	1286	1296	1306	1316	1326	1336	1346	1356	1367
$V''$	649.47	638.34	627.21	616.08	604.94	593.80	582.65	571.49	560.33	549.16
	3.913	5.703	8.492	12.94	20.22	32.39	53.56	91.40	161.4	296.4
$V/M$	0.441	0.639	0.944	1.427	2.213	3.517	5.774	9.780	17.14	31.22
	111.3	73.56	47.53	29.97	18.41	11.00	6.568	3.567	1.927	1.000

By way of contrast we may take another example which corresponds more nearly with the variation of the efficiency in practice, and gives a much simpler method of calculation and of subdivision of the heat-drop.

*Example 2.* With the same initial and final data, and  $F = 0.60$ , divide the pressure-range into ten equal intervals by ratio. Assuming that the work done is the same in each wheel-chamber, find the stage efficiency, (1) for supersaturated, (2) for saturated steam.

Since  $\log 165/1 = 2.21748$ , the logarithm of the pressure-ratio for each nozzle is 0.22175, or the ratio  $P'/P''$  is 1.6668 for successive chambers. The corresponding pressures are given in line 1 of the next table. Neglecting external loss of heat, the actual heat-drop in each chamber is by hypothesis 10.853, which gives the values of  $H''$  in the next line. Assuming that after passing the wheel, the steam has recovered its equilibrium state of saturation, the values of the final volume  $V''$  in each chamber are deduced from those of  $H''$  by the usual relation for wet steam, and are given in the next line. To find the adiabatic drop  $DH_0$  in case (1) for supersaturated steam, we may neglect  $b$  as being beyond the limits of possible accuracy, and take the formula,  $a(n+1)P_0V_0(1-(P/P_0)^{a/hs})$ , given in Chapter IX, equation (85). Since  $P/P_0$  is constant and equal to  $1/1.6668$  for each stage, the expression for  $DH_0$  reduces to the convenient form  $P_0V_0/20.185$ . For the first nozzle,  $P_0 = 165$ , and  $V_0 = 2.781$ . For the next nozzle  $P_0 = P_1$ , and  $V_0 = V_1''$ , and so on for successive nozzles.

The resulting values of  $f$  for each stage are obtained by dividing

10.858 by the successive values of  $DH_s$ . These show, in contrast with the preceding example, a rapid increase of efficiency in the later stages. The increase may appear excessive, but is probably exceeded in practice in many cases, especially in small machines, which are apt to be very inefficient in the early stages. On the other hand, in the later stages, efficiencies of 0.80 appear to have been reached under favourable conditions.

To find the corresponding nozzle-areas, it is first necessary to calculate the values of  $V'$  for each stage. These are obtained from the formula for supersaturation which gives the ratio

$$V''/V' = (P'/P'')^{10/13},$$

so that each  $V'$  is obtained by simply multiplying the previous  $V''$  by the constant 1.4813. The values of  $X'/M$  follow from the formula  $144V'/U'$ , or  $218.8V''/U'$ .

(2) If the adiabatic equation for saturated steam is employed for finding the heat-drop and the volume  $V'$ , the calculation is a little more troublesome, since  $G$  and  $\Phi$  are required, but the results, as shown in the next five lines of the table, do not differ materially in character. In either case the stage efficiency  $f$  must vary nearly as  $1/PV$  if  $DH''$  is proportional to  $\log (P'/P'')$ . The actual values of  $f$  are a little smaller, and those of  $U'$ ,  $V'$ , and  $X'$ , a little larger, for saturated than for supersaturated steam; but it is probable that the supersaturated condition more nearly represents the facts of the case in rapid expansion, and it has the additional advantage of simplifying the calculation.

*Example 3.* Another assumption that appears to be often made in designing turbines is that of equal expansion ratios by volume between successive stages. This may be combined with the assumption of equal pressure ratios, by using a formula of the type  $PV^\gamma = K$ , or  $PV = kP^m$ , for the expansion curve. The value of the index  $m$  or  $\gamma$  is selected to fit the same final values of  $H''$  and  $V''$  as in the previous example with  $F = 0.60$ . The values of  $V''$  are then calculated as in line 2, and those of  $H''$  deduced from  $V''$ , giving the nearly constant differences for  $DH''$  shown in the next line. The values of  $DH_s$  supersaturated differ very little from those in Example 2 (1). Those of  $f$  are all a little higher, but the expansion curves assumed in Examples 2 and 3 are so nearly coincident for saturated steam that the results differ remarkably little in character.

It will be seen that the assumption of a formula of the type  $PV^\gamma = K$ , for the relation between the values of  $P$  and  $V$  in suc-

Table II. Results for Example 2.

No.	1	2	3	4	5	6	7	8	9	10
$P$	99.02	59.43	35.66	21.40	12.84	7.710	4.626	2.777	1.666	1.000
$H''$	656.71	645.85	635.00	624.14	613.29	602.43	591.58	580.73	569.87	559.02
$V''$	4.447	7.111	11.37	18.17	29.02	46.36	74.02	118.3	189.2	302.1

(1) For supersaturated steam.

$DH_{\phi}$	22.74	21.82	20.94	20.09	19.27	18.47	17.71	16.97	16.28	15.62
$f$	0.477	0.497	0.518	0.540	0.563	0.588	0.614	0.640	0.667	0.695
$U'$	1430	1400	1372	1344	1317	1290	1262	1235	1210	1185
$V'$	4.120	6.588	10.54	16.84	26.91	42.99	68.68	109.6	175.2	280.2
$X'/M$	0.414	0.678	1.108	1.804	2.940	4.800	7.840	12.78	20.80	34.10

(2) For saturated steam.

$DH_{\phi}$	23.32	22.36	21.52	20.64	19.81	18.99	18.24	17.49	16.78	16.12
$f$	0.465	0.485	0.504	0.526	0.548	0.572	0.595	0.620	0.647	0.673
$U'$	1450	1420	1392	1363	1336	1308	1282	1256	1230	1205
$V'$	4.335	6.947	11.12	17.81	28.50	45.59	72.94	116.7	186.8	299.1
$X'/M$	0.430	0.704	1.151	1.882	3.071	5.020	8.194	13.39	21.87	35.74

Table for Example 3.  $PV^m = K$ , or  $PV = kP^m$ , where  $m = 1 - 1/\gamma$ .

$P$	99.022	59.427	35.664	21.402	12.845	7.7089	4.6264	2.7765	1.6663	1.000
$V''$	4.4429	7.1002	11.347	18.134	28.979	46.312	74.012	118.28	189.02	302.08
$H''$	656.28	645.19	634.32	623.62	613.02	602.43	591.78	581.02	570.12	559.02
$DH''$	11.30	11.07	10.87	10.70	10.60	10.50	10.45	10.76	10.90	11.10
$DH_{\phi}$	22.73	21.80	20.91	20.05	19.23	18.44	17.69	16.97	16.27	15.61
$f$	0.497	0.508	0.520	0.534	0.551	0.574	0.602	0.634	0.670	0.711

cessive stages, fits very closely with the hypothesis that equal pressure and expansion ratios give a nearly constant value of the heat-drop  $DH''$ , or the actual work performed in each stage, in the case of saturated steam. Or conversely, that if equal values of the heat-drop  $DH''$  are assumed, the successive values of the volume for saturated steam will show a nearly constant expansion-ratio for a constant pressure-ratio, as is easily seen by comparing the values of  $V''$  given in Examples 2 and 3. The difference is so small that careful calculation is required to detect it.

The most troublesome part of the calculation in Example 2 is the deduction of the values of  $V''$  from those of  $H''$  by the tables for saturated steam. Since the exact state of the steam is uncertain, it is permissible in the present case to simplify the calculation by assuming a constant expansion-ratio for  $V$ , which gives a constant ratio for successive values of  $PV$ , and  $DH_{\phi}$ , and  $V'$ , and  $f$ , and  $U'$ . It is not, however, permissible to assume, as is sometimes done, that the expansion-ratio is the same as the pressure-ratio. This would be equivalent to assuming the expansion curve  $PV = K$ ,

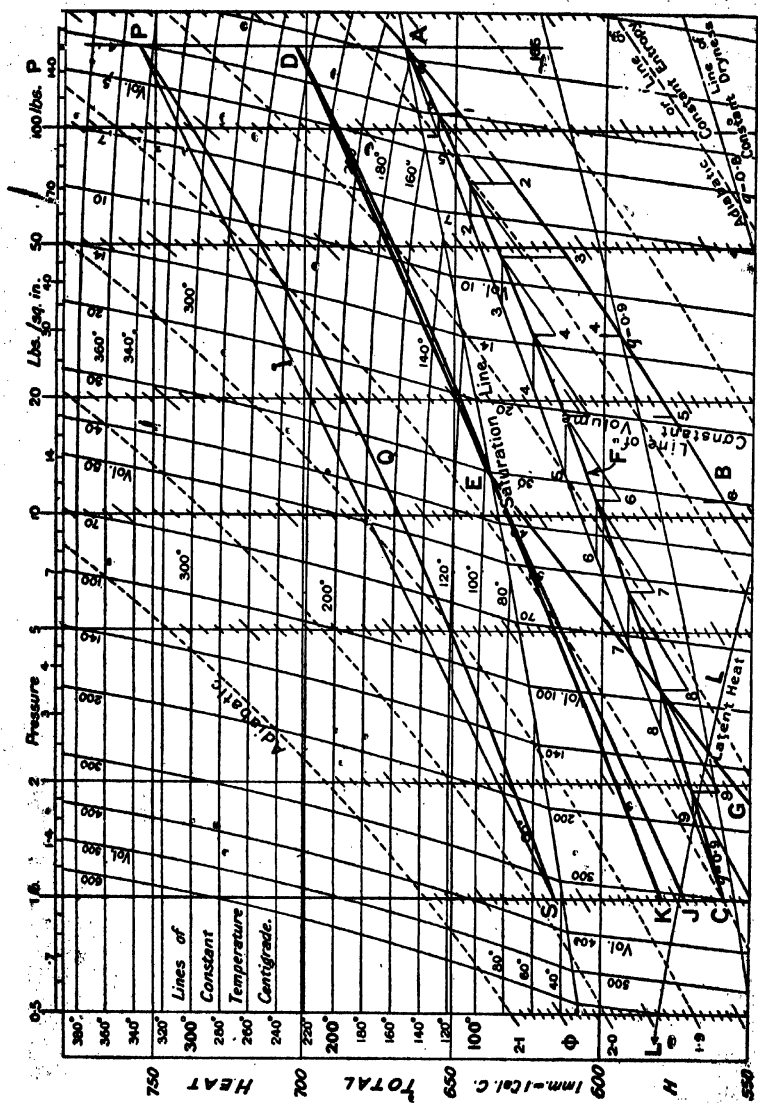


Fig. 32. Characteristic Curves on the  $H \log P$  diagram.

with  $\gamma = 1$ , and would lead to an absurd value of the final volume and  $H''$ . It is essential to calculate the value of the index  $\gamma$  to fit the final value of the volume deduced from the given value of  $F$ .

In Example 8, it is much more troublesome to deduce accurate values of  $H''$  from  $V''$ , than to deduce  $V''$  from  $H''$  in Example 2; because the rapid variation of  $V$  makes interpolation more difficult, and because it is necessary to work both  $V''$  and  $V$ , to at least five significant figures, in order to obtain consistent values for the small difference  $DH''$ , and to show the nature of the systematic variation. The result is instructive as showing that the assumption of an expansion curve of the type  $PV^\gamma = K$ , cannot possibly be consistent with a constant value of the stage efficiency  $f$  for saturated steam.

*Graphic Representation on the  $H \log P$  Diagram.* The pressures required in Example 1 are readily found on the diagram by dividing the heat-drop along the adiabatic AB into ten equal parts at the points 1, 2, 3, etc., of which the first six only are shown in the annexed Fig. 82. The corresponding points on the actual expansion curve for  $F = 0.60$  (constant), are found by reducing the adiabatic heat-drop at each point in the constant ratio 0.60. The points representing the final states lie on the continuous curve AFC, which is the same as for continuous expansion (Chapter XII, Example 6), at constant  $F$ ; but the actual expansion in ten discontinuous steps follows a zigzag course, consisting of adiabatic steps such as A 1, representing the expansion in the first nozzle, followed by vertical steps, representing loss of heat-drop in passing through the wheel, which bring the final state back to the curve AFC before the next adiabatic step. In order to avoid confusion, these zigzags due to discontinuity of expansion, are not shown on the other curves in the figure.

The straight line AC joining the initial and final states, represents the final states in each chamber according to the hypothesis of Example 2. The heat-drop is the same, namely 10.858, in each stage as in Example 1, but the pressures differ considerably, as shown by the horizontal lines joining pressures corresponding points on the straight line AC and the curve AFC. The pressure at point 5 on AFC is greater than that at point 5 on AC by 43 per cent.

The curve representing the case of Example 8 coincides so closely with the straight line AC that the differences cannot be shown clearly on the scale of the diagram. The pressures at corresponding points are the same. The curve for Example 8 intersects

the straight line AC at point  $\delta$ , the maximum difference at point 8 being only 0.7 cal. It appears that a straight line on the  $H \log P$  diagram represents very fairly on the average the characteristic of a turbine when the steam is assumed to be in the state of saturation throughout the expansion. But this is not the case when the steam is superheated or supersaturated, and changes in the form of the characteristic may be expected when the state changes from dry to wet.

**141. Subdivision of the Heat-Drop for Given Values of  $f$ .** There is no great difficulty in finding the subdivision of the pressure-range or the heat-drop on similar assumptions to correspond with any arbitrary values of  $f$  for the separate wheels. It is necessary, however, in this case, to calculate the final state in each stage before proceeding to the next, and some adjustment of the velocity, or the number of stages, is usually required to make the final state fit the given data. The most appropriate method in each case will depend on the given conditions. As a simple illustration, we may take the case of finding the subdivision of the pressure-range, and the required nozzle-areas, for ten stages, when the velocity and efficiency are assumed to be the same for all stages, in which case both  $DH_0$  and  $DH''$  must be the same for all. The pressure-drop is deduced from  $DH_0$  instead of *vice versa*. If the final state is given by  $F$  and  $p$ ,  $DH''$  is known for each stage, and  $DH_0 = DH''/f$ , but the value of  $f$  requires adjustment to fit with that of  $F$ , by a method explained in a later section. On the other hand, if the final value of  $H''$  alone is given, in place of  $F$  and  $p$ , an arbitrary value of  $f$  may be selected.

*Example 4.* Divide the pressure-range from 165 lbs. abs. (dry sat.) to 1 lb. into ten parts to give the same velocity and efficiency in each, assuming that  $F = 0.60$ , (1) for saturated, (2) for super-saturated steam.

Since  $F = 0.60$ , the actual heat-drop  $DH''$  in each stage must be 10.858, as previously calculated, but the required values of  $f$  to fit with the given value of  $F$ , will be different in cases (1) and (2).

(1) In the case of saturated steam, the required value of  $f$  is 0.560, and the value of  $DH_0$  for each stage is 19.88, giving  $U' = 1322$ . The temperature drop for the first nozzle is calculated from the equation

$$19.88 = \Phi_0 Dt - DG, \dots\dots\dots(2)$$

(as in Example 1, above) which fixes the final state in the first

chamber in conjunction with the given value of  $DH''$ . The final value of  $\Phi''$ , required for the next nozzle, is easily obtained, since

$$\Phi'' - \Phi_1 = (19.88 - 10.858)/T = 8.527/T. \dots\dots(8)$$

The temperature for the next chamber may then be found.  $V'$  and  $X'/M$  are also found as in Example 1, and  $p$  is obtained from  $t$ .

(2) In the case of supersaturated steam, a higher value of the stage efficiency  $f$  is required to fit with the given value of  $F$ , on account of the loss due to supersaturation. The required value in the present case is 0.576, but the value 0.575 was estimated, and employed in the calculation, which has the effect of making the final pressure come out a little too low. The difference 0.016 in  $f$  for the same  $F$ , is far from representing the limit of possible loss due to supersaturation, because we have supposed the steam restored to the state of saturation at the end of each stage. This might approximately be the case at low speeds in large marine turbines, but in many cases the whole expansion from boiler to condenser pressure is completed in less than the hundredth part of a second, and the temperature of the steam is probably nearer the SS limit throughout the expansion, which would involve a much greater reduction in the efficiency, or a still higher value of  $f$  for the same  $F$ . Taking  $f = 0.575$  gives  $DH_s = 18.88$  for the adiabatic heat-drop per stage, and  $U = 1304$  for the velocity. The pressure-drop is given by the equation

$$1 - (P/P_0)^{3/13} = 3 \times 18.88/13aP_0V_0 = 42.86/P_0V_0, \dots\dots(4)$$

neglecting  $b$ , as is permissible in the case of supersaturated steam. The calculation is a little more troublesome than in Example 2, because it has to be repeated for each stage. Having found  $P$ , the value of  $V''$  is taken as in (1) for saturated steam with the given value of  $H''$ . The pressure ratio for the next nozzle is then found from the product  $pV''$ . The initial value of  $V'$  in each stage is deduced from the final value of  $V''$  in the previous stage by the relation,  $V' = V''(P'/P'') (P''/P')^{3/13}$ , which is put in this form because the last factor has already been calculated.

If the results in Examples 1, 2, 3, and 4, are compared with those previously given in the corresponding cases for continuous expansion in Chapter XII, Examples 3, 5, 6, it will be seen that there are slight characteristic differences between the two sets of examples, but that the general effects of the assumptions  $F$  con-



stant, or  $f$  constant, or  $PV = kP^m$ , are very similar, whether for continuous or discontinuous expansion. The manner in which  $f$  varies from stage to stage produces a much more important effect on the pressure-distribution and on the proper dimensions of the nozzles, etc. than discontinuity of expansion.

Table III. Results for Example 4.

(1) Saturated steam.  $F = 0.60$ ,  $DH'' = 10.853$ ,  $f = 0.560$ ,  $DH_\phi = 19.88$ ,  $U = 1822$  (all constant throughout the expansion).

No.	1	2	3	4	5	6	7	8	9	10
$H''$	656.71	645.85	635.00	624.15	613.30	602.44	591.59	580.74	569.88	559.03
$t$	167.45	160.30	154.05	148.54	143.76	139.62	136.11	133.15	130.71	128.74
$\phi''$	1.5884	1.6085	1.6294	1.6512	1.6739	1.6975	1.7217	1.7472	1.7735	1.8010
$V''$	4.013	5.994	9.060	14.04	22.08	35.44	58.12	97.56	167.9	297.1
$X/M$	0.437	0.653	0.987	1.530	2.406	3.862	6.333	10.63	18.30	32.38
$p$	108.2	69.71	44.21	27.50	16.78	10.02	5.850	3.335	1.853	1.000

(2) Supersaturated.  $H''$  same,  $f = 0.575$ ,  $DH_\phi = 18.88$ ,  $U = 1804$ ,  $F = 0.599$ .

$p$	108.5	70.14	44.51	27.72	16.91	10.08	5.874	3.335	1.842	0.988
$V''$	4.073	6.063	9.189	14.17	22.28	35.83	58.87	99.20	171.7	306.0
$V'$	2.837	5.700	8.602	13.23	20.73	33.16	54.30	90.98	156.6	277.2
$X/M$	0.424	0.669	0.950	1.461	2.289	3.661	5.995	10.05	17.29	30.60

Results for Example 5. Superheated.  $P_0 = 165$ ,  $t_0 = 350^\circ \text{C.}$ ,  $H_0 = 756$ ,  $F = 0.643$ ,  $DH'' = 14.00$ ,  $f = 0.568$ ,  $DH_\phi = 24.645$ ,  $U = 1490$  (all constant).

No.	1	2	3	4	5	6	7	8	9	10
$H''$	742	728	714	700	686	672	658	644	630	616
$P$	112.7	75.49	49.39	31.62	19.55	11.74	6.797	3.772	1.993	0.993
$V''$	5.335	7.543	10.89	16.05	24.27	37.73	60.53	100.7	174.9	319.3
$X/M$	0.516	0.729	1.052	1.551	2.346	3.646	5.850	9.730	16.90	30.88
$t''$	318.61	287.51	256.57	225.50	195.32	165.46	135.40	105.51	75.74	46.07

**142. The Case of Superheated Steam.** The method of calculation in the case of superheated steam is very similar to that in the case of supersaturated steam when similar data are given. The chief difference is that, if the final state in any stage is dry, the volume  $V''$ , if required, can easily be deduced from  $H''$  and  $P$  which saves a great deal of trouble and reference to the tables. But it is seldom necessary to calculate  $V''$  in the case of dry steam, because  $DH_\phi$  for the next stage can be deduced directly from  $H''$ .

by the alternative formula in terms of  $H$  for dry steam, IX (82), or Steam Tables, § 198, which cannot be employed when the steam is wet, because the relation between  $H$  and  $V$  is different for wet steam. The value of  $H''$  in any stage shows at once if the steam is saturated. The values of  $t$  are not required in the calculation for superheated steam, but are given in the last line of the table because they are useful in practice for comparison with observed temperatures.

In order to avoid the difficulty of the transition from dry to wet steam we will take first a case in which the steam is superheated throughout the expansion, but in which the calculation is otherwise similar to Example 4 (2).

*Example 5.* If the initial steam is superheated to  $350^{\circ}\text{C}$ ., divide the same pressure-range to give equal velocity and work in all stages with an actual heat-drop of 140 cal. C.

In this case  $H_0 = 756$ , and the successive values of  $H''$  are given at the head of the table. The adiabatic heat-drop to 1 lb. is 217.72, and the value of  $F$  is 0.643 approximately. Since  $\Phi_0 = 1.7845$ , the final state on the adiabatic is saturated. The required value of  $f$  is 0.568 to the same order of accuracy as  $F$ , giving

$$DH_{\phi} = 14.00/0.568 = 24.645,$$

and  $U' = 1490$  (F.P.C.). The successive values of  $P$ , given in the next line of the table, are obtained from the equation for the adiabatic heat-drop for dry steam in terms of  $H$ , which is inverted to give the ratio  $P/P_0$ , when  $DH_{\phi}$  is given as 24.645, thus

$$1 - (P/P_0)^{3/13} = (24.645 - ab(P_0 - P))/(H_0 - B - abP_0) \dots (5)$$

The terms depending on  $b$  are here taken into account in order to make the results exactly consistent with the tables, but since  $ab$  is only 0.00165, the correction is very small, and gives little trouble. The successive values of  $H_0$  required in the formula are those of  $H''$  already given, but the ratio  $P/P_0$  is not constant, and has to be worked out for each stage in succession\*.  $V''$  is easily found from  $H''$ , but is not required in the calculation. The values of  $V'$  required for the nozzle areas are given by the formula

$$V' - b = 2.2486 (H_0 - B - abP_0) (P/P_0)^{3/13} / P, \dots (6)$$

in which  $H_0$ ,  $P_0$ , are the initial values for the nozzle considered,

\* The calculation of  $P/P_0$  from  $(P/P_0)^{3/13}$ , or vice versa, is most easily effected by employing a table, such as that given in § 135, but with more numerous steps in the required interval.

and the separate factors have already been found in calculating  $P$ . The nozzle areas are directly proportional to  $V'$ , since  $U'$  is constant. It will be observed that the final area is nearly the same as in the previous example, but the initial areas are about 20 per cent. larger. This shows that, if the nozzle areas are right for saturated steam, there will be an appreciable change in the distribution of pressure and velocity when the steam is superheated. But since similar modifications occur when the load, or the pressure, is changed, the design is necessarily a compromise, unless the machine is required to run always under the same conditions.

It is instructive to compare the effect of superheat, according to the assumptions here made for discontinuous expansion, with the effect calculated in the preceding chapter (§ 185) for the same case with continuous expansion. For the same value,  $F = 0.648$ , of the relative efficiency, the values of the stage efficiency in the case of superheated steam are,  $f = 0.5686$  for ten stages, and  $f = 0.5541$  for continuous expansion. For steam initially saturated, with the same pressure range and  $F = 0.60$ , we have  $f = 0.5551$  for continuous expansion, and  $f = 0.560$  for ten stages, if the steam is saturated in the nozzles, but  $f = 0.576$  if the steam is supersaturated. For the same value of  $f$  in each case, the improvement in  $F$  due to superheat is appreciably less for ten separate stages than for continuous expansion under the same conditions. If the steam is supersaturated in the nozzles only, there is an additional improvement due to superheat amounting to 8.5 per cent. as compared with the usual assumption of saturation. There is so much evidence in favour of supersaturation in the throat of a nozzle, that this 8.5 per cent. may be regarded as a lower limit of the effect of supersaturation. The upper limit of the effect was found to be nearly 9 per cent. in the same case for continuous expansion with the steam at the SS limit. A similar increase of the effect would be found in discontinuous expansion if the steam were assumed to be at the SS limit throughout, in place of being restored to the state of saturation at the end of each stage.

The improvement in  $F$ , due to the higher value of the reheat factor in the case of superheated steam, and due to the elimination of supersaturation loss, is *additional* to the improvement in absolute thermal efficiency due to the higher temperature, and is relatively more important even at the lower limit of supersaturation loss here assumed. Thus the thermal efficiency of the Rankine cycle in Example 5 is 0.808, while in Example 4 it is 0.287, or 5 per cent.

less. With the same stage efficiency,  $f = 0.572$  in both cases, Example 5 shows an improvement over Example 4 of nearly 9 per cent. in  $F$ , and of 15 per cent. in absolute thermal efficiency, which results chiefly from the improvement of  $F$ .

The expansion curve of Example 4, representing the case  $f$  constant, when drawn on the  $H \log P$  diagram, as in the preceding Fig. 82, lies about midway between the curve AFC, representing the case  $F$  constant, and the straight line AC, but there is no simple geometrical method of constructing the curve of constant  $f$  on the diagram, short of calculating the values of  $DH$  and plotting the curve. The curve PQS in the upper part of the figure has been drawn in this way to represent the case of Example 5, for highly superheated steam with  $f$  constant, but there is no advantage in using the diagram in such a case, except as an illustration of the general nature of the curve. The curve of constant  $F$  between the same initial and final states would lie a little below the curve of constant  $f$ , and could be deduced graphically from the adiabatic as in Example 1. But the expansion curve of any actual machine would lie *above* the curve PQS, since  $f$  is always less in the early than in the later stages of expansion. It would be very difficult to draw such a curve with different values of  $f$  in each stage except by calculating the values of the heat-drop successively for each stage.

An appropriate use of the diagram in the case of *superheated* steam would be for plotting the actual expansion curve from *observed* values of  $P$  and  $t$  in each stage. This would give useful information with regard to the variation of the stage-efficiency, but does not appear to have been attempted hitherto on account of the difficulty of measuring the temperatures, the uncertainty of the values of  $H$ , and various other reasons.

The following Examples 6 and 7, in which half the expansion curve is below the saturation limit, are illustrated in Fig. 82, by the straight line DEJ, representing the characteristic

$$H - B'' = k \log P,$$

and by the broken line DEG, representing the expansion curve  $PP' = K$ , showing a discontinuity at the point E where the state changes from superheated to saturated. The continuous curve DEK, which lies slightly below the straight line from D to E, represents the characteristic  $H - B'' = kP^{0.05}$  of Example 7, with  $F = 0.64$ , which affords a more probable solution of a case of this

kind in practice. It is important to realise that a curve of the type  $PV^\gamma = K$ , with a single value of  $\gamma$  throughout, cannot be employed if there is a change in the state of the steam.

*Example 6.* With an initial temperature of  $250^\circ\text{C}$ ., if the same pressure range is divided into ten equal intervals by ratio, and the steam is just saturated at the end of stage 5, find the variation of  $f$ , if  $DH''$  is the same in each stage.

Initial state,  $t_0 = 250^\circ\text{C}$ .,  $H_0 = 708.84$ ,  $\Phi_0 = 1.64318$ ,  $G_0 = 157.40$ ,  $V_0 = 8.2737$ .

Pressure ratio, 1.6668 per stage,  $P_5 = 12.845$ ,  $H_5'' = 637.80$  (dry saturated).

Heat-drop per stage,  $DH'' = 13.208$ , adiabatic drop, 194.05,  $F = 0.6806$ .

Superheated,  $DH_\phi = 0.11115 (H_0 - B - abP_0) + ab (P_0 - P)$ , (7)

Supersaturated,

$$DH_\phi = 0.04953 P_0 V_0 \text{ (neglecting } b \text{ at low pressures). } \dots (8)$$

The values of  $V''$  are obtained from those of  $H''$  by the formulae for dry and wet steam respectively. Those of  $V'$  in each stage are found by multiplying the  $V''$  of the previous stage by the constant factor 1.481. The results are compared in the following table with those obtained by assuming a formula of the usual type,  $PV^\gamma = K$ , instead of taking equal values of  $DH''$  per stage.

Table of results for Example 6. Superheated,  $t_0 = 250^\circ\text{C}$ .

No.	1	2	3	4	5	6	7	8	9	10
$H''$	690.63	677.42	664.22	651.01	637.80	624.59	611.38	598.18	584.97	571.76
$V'$	5.101	8.069	12.61	19.61	30.368	48.29	76.79	122.2	194.4	309.6
$V''$	4.849	7.556	11.95	18.68	29.05	44.98	71.54	113.8	181.0	288.0
$DH_\phi$	26.74	25.24	23.75	22.27	20.79	19.32	18.44	17.60	16.80	16.06
$f$	0.494	0.523	0.556	0.593	0.635	0.684	0.716	0.750	0.786	0.823
$U'$	1552	1508	1463	1417	1369	1320	1289	1260	1230	1203
$X'/M$	0.450	0.722	1.176	1.898	3.056	4.907	7.902	13.00	21.19	34.47

Taking $V''$ from $PV^\gamma = K$ , with $\gamma = 1.14612$ , and deducing $H''$ from $V''$ .										
$V''$	5.1111	7.9798	12.458	19.451	30.368	47.413	74.024	115.57	180.44	281.71
$H''$	689.03	675.03	661.84	649.44	637.80	614.77	591.86	569.05	546.41	523.93
$DH''$	14.81	13.99	13.19	12.40	11.65	23.02	22.91	22.81	22.64	22.48
$DH_\phi$	26.74	25.06	23.48	22.01	20.62	19.34	18.11	16.96	15.90	14.99
$f$	0.553	0.558	0.562	0.564	0.565	1.19	1.27	1.34	1.42	1.50

The second part of the above table is intended to illustrate the fact that it is not possible to assume a formula of the type  $PV^\gamma = K$ , with a constant value of  $\gamma$ , when part of the curve is dry and part

wet, because this gives a discontinuity in the curve at saturation, and leads to impossible values of  $f$  at lower temperatures, besides being very inconvenient for calculation.

The two assumptions here made for the expansion, though agreeing closely in the case of saturated steam, are entirely discordant when applied to a case in which the steam is initially superheated. If we keep the assumption that  $DH''$  is the same in each stage for equal pressure ratios, a fair approximation to the expansion curve can be obtained by using two formulae of the type  $PV = kP^m$ , with different values of  $m$ , denoted by  $m'$  and  $m''$ , for the superheated and saturated portions. In this case  $f$  will be constant and equal to  $18m/8$  for the superheated portion, but will increase from stage to stage in the saturated part of the curve.

The assumption made for  $DH''$  in Example 6, though fairly satisfactory in many cases for saturated steam, is too inelastic in the general case, and gives highly improbable results with initial superheat. For these reasons it is preferable to employ the more general type of characteristic,  $H - B' = kP^m$ , as illustrated in the previous chapter, which gives a very simple expression for  $f$ , and is capable of representing any continuous variation of  $f$  with a reasonable degree of approximation.

In applying this formula the most convenient methods are, either (1) assume equal division of work (i.e. equal values of  $DH''$ ), and find the values of the constants  $m$  and  $B'$  to suit the desired range of variation of  $f$ , as illustrated in the previous chapter, or (2) divide the pressure-range into equal intervals by ratio, and adjust the values of the constants to make the curve pass through some point near the middle of the range in addition to the initial and final values. In case (1) values of the required quantities at intermediate points are obtained by logarithmic interpolation as previously explained. In case (2), if  $H_0$ ,  $H'$ ,  $H''$ , are three values of  $H$  corresponding to the initial and final states and to the geometric mean pressure  $P'$ , we have the obvious relations

$$(H_0 - H')/(H' - H'') = (P_0/P')^m = (P'/P'')^m. \dots\dots(9)$$

The heat-drop in this case is divided into parts forming a geometrical progression with a common ratio, which facilitates calculation. The previous example affords a convenient illustration of this method of applying the formula, since  $H'$  is given at the mean point  $P'$ , but the values of  $DH''$  per stage will no longer be equal.

**Example 7.** With the same initial data as in the previous example, find the variation of  $f$  by the formula  $H - B'' = kP^m$ , if  $F_s = 0.64$ , and the steam is just saturated at the end of stage 5.

The whole heat-drop is here  $194.05 \times 0.640 = 124.20$  cals. C. The given heat-drop to stage 5 is 66.04. That from 5 to 10 is 58.16. The logarithm of the ratio 66.04/58.16 is  $m$  times the logarithm of the ratio  $P_0/P_5$ , namely 1.10874; whence  $m = 1/20$  very nearly, and the logarithm of the ratio for successive values of  $DH''$  is 0.0110874. Dividing the whole heat-drop into ten parts with this common ratio we very easily obtain the following results.

Table V. Example 7.  $F = 0.640$ ,  $H_s'' = 637.80$ ,  $m = 1/20$ .

No.	1	2	3	4	5	6	7	8	9	10
$P$	99.02	59.43	35.66	21.40	12.84	7.709	4.626	2.776	1.666	1.000
$DH''$	15.89	13.54	13.21	12.86	12.54	12.23	11.92	11.62	11.33	11.04
$H''$	689.95	676.41	663.20	650.34	637.80	625.57	613.65	602.03	590.70	579.66
$V''$	5.131	8.030	12.54	19.54	30.37	48.38	77.12	123.0	196.5	314.1
$DH_+$	26.76	25.17	23.64	22.16	20.72	19.32	18.47	17.69	16.92	16.22
$f$	0.619	0.538	0.559	0.580	0.606	0.632	0.645	0.657	0.670	0.681

With the exception of the subdivision of the heat-drop into equal logarithmic intervals in place of equal differences, the method of calculation is precisely the same as for Example 2 in the case of supersaturated steam. A comparison of the results appears to represent the effect of superheating in a fairly satisfactory manner, on the assumption that  $f$  is increased by reduction of friction. The relative efficiency  $F$  is raised from 0.60 to 0.64, while the stage efficiency  $f$  remains nearly unaltered in the later stages, when the steam is wet, but is raised by the nearly constant quantity 0.042 in all the superheated stages.

In an actual turbine, the efficiency may vary from stage to stage in an irregular manner depending on differences of wheel construction or diameter. Such variations cannot be represented by the formula, which can only represent systematic and continuous variation. Admitting this restriction, the formula has a considerable range, and is easily adaptable to suit different cases.

**143. Discontinuous Expansion with  $f$  Constant.** As an illustration of the adaptability of the formula, we may take the case in which it is required to find the characteristic curve when  $f$  is assumed constant.

In the case of dry steam, the expression for the adiabatic heat-drop, if  $b$  is neglected, is exactly similar to that given by the empirical formula for the actual heat-drop, namely,

$$(H_0 - H'')/(H_0 - B'') = 1 - (P''/P_0)^m, \dots\dots\dots(10)$$

but in the formula for the adiabatic heat-drop the empirical constant  $B''$  is replaced by  $B = 464$  cal. C., and the empirical index  $m$  by  $8/18$ . It follows that if  $B''$  is taken as 464, and if  $m$  is taken to fit the final state, the resulting values of  $f$  will be exactly constant, if  $b$  is neglected in the equation of the adiabatic. The neglect of  $b$  makes so little difference in the adiabatic, that the values of  $f$  will be sufficiently nearly constant for all practical purposes even if the exact values of the adiabatic heat-drop are employed. The required value of  $m$  is obtained in any case by inserting in the above formula in place of  $H''$  and  $P''$ , the values  $H_F$  and  $P_F$  corresponding to the final state given by the value of  $F$ .

For the case in which  $f$  is constant, and  $B'' = B$ , the values of  $F$  and  $f$  are given by the expressions

$$f = (1 - r^{m/N})/(1 - r^{8/18N}), \text{ and } F = (1 - r^m)/(1 - r^{8/18}), \dots\dots\dots(11)$$

where  $N$  is the whole number of stages, and  $r^{1/N}$  the pressure-ratio per stage.

Thus in Example 5,  $N = 10$ ,  $H_0 = 756$ ,  $H_F = 616$ ,  $r = 1/165$ . If  $B'' = B = 464$ , we have  $m \log r = \log (152/292) = -0.28854$  from (10),  $\log r^{m/N} = -0.028854 = 1.971646$ , whence  $r^{m/N} = 0.08680$ . Similarly  $r^{8/18N} = 0.88885$ . Whence

$$f = 0.06320/0.11115 = 0.5686. \dots\dots\dots(12)$$

The value taken in the calculation was 0.568, but should have been a little larger, since  $b$  was not neglected. The advantage of using the empirical formula in such a case is that all the intermediate values of  $P$  and  $V$  can be worked out by logarithmic interpolation from the initial and final states, as fully illustrated in Example 8 of the preceding chapter, without going through the very troublesome process of calculating each stage in succession by means of the exact formulae, and with almost equal accuracy, since only  $b$  is neglected.

In the case of supersaturated steam, the method of calculation is precisely the same so long as the steam is dry. But when it has reached the supersaturation limit, the value  $B = 464$  no longer applies, since the relation between  $H$  and  $V$  is different for wet



steam. The value of  $V$  in the final state must first be calculated from that of  $H$  by the appropriate formula, according as the final state is assumed to be either at the saturation limit or the super-saturation limit. The value of the index  $m$  and the constant  $B''$  are then obtained from the relations

$$(H_F - B'')/(H_0 - B'') = r^m = P_F V_F / P_0 V_0. \dots\dots(18)$$

If dry supersaturated expansion in the nozzles is assumed, as is most appropriate when the initial state of the steam for each nozzle is taken to be at the ordinary saturation limit, as in Example 4, the constant value of  $f$  required for each stage is given by the expression

$$f = (1 - r^{m/N})_s (H_0 - B'') / (H_0 - B) (1 - r^{3/13N}). \dots\dots(14)$$

Thus in Example 4 the required values of the constants are.

$$r^m = 0.6584, B'' = 349.8, f = 0.575. \dots\dots\dots(15)$$

If the supersaturation limit is assumed in the later part of the expansion for the final state in each stage (since there is very little time for the recovery of complete equilibrium while the steam is passing through the blades), adiabatic expansion at the super-saturation limit, as calculated in Chapter X, may appropriately be assumed in the nozzles as the other extreme. The final value of  $H$  given by  $F$  remains the same, but the corresponding value of  $V$  is taken at the supersaturation limit. The constants  $m$  and  $B''$  may be calculated as before, but will no longer give so good an approximation to the curve of constant  $f$  because the first part of the expansion, starting with dry saturated steam, is not at the supersaturation limit like the rest. A constant value of  $f$  could not be expected in practice under such conditions, unless the dimensions were specially adjusted to suit. A similar result follows if part of the expansion is taken in the superheated and part in the saturated region. But such problems are rather of academic than practical interest, since a single continuous curve cannot accurately represent both states without impracticable complexity.

The value of  $m$  is calculated from the condition  $PV/P_0V_0 = r^m$ , because this is the condition required to make the initial and final values of  $f$  equal, § 181, or to make the successive values of the adiabatic drop  $DH$ , approximately proportional to those of  $DH''$

given by the expansion curve  $H'' - B'' = kP^m$ . But the formula  $PV/P_0V_0 = f^m$  does not represent the expansion curve, as commonly assumed, and would give values of  $DH''$  quite inconsistent with the desired result  $f = \text{constant}$ , as shown in Example 3. The two curves are so widely separated on the diagram as to give very different results for the small difference  $DH''$ , but the values of  $PV$  change so slowly with  $H$  at constant  $P$  that they remain nearly the same for both curves at the same pressure. The formula  $H'' - B'' = kP^m$  represents the curve of constant stage efficiency sufficiently closely for all practical purposes, but if more exact results are required, they may be obtained by the method of Examples 4 and 5.

In the case of saturated steam, if an adiabatic of the type  $PV^\gamma = K$  is assumed, with  $\gamma = 1.1804$ , the expression for the adiabatic heat-drop is the same in form as for supersaturated steam, but with the index coefficient  $3/26^*$  in place of  $3/13$ . The value of  $m$  required to make  $f$  constant in the expansion formula  $H - B'' = kP^m$ , may be obtained in the same way from the condition  $PV/P_0V_0 = f^m$ , and has the same value as for supersaturated steam for the same initial and final states, because we have merely changed the expression for  $DH_\phi$  by inserting a different value of the constant, e.g. from  $PV/20.185$  for supersaturated to  $PV/19.605$  for saturated steam under the conditions of Example 4. The required value of  $f$  is changed in the same ratio as the constant, namely, from 0.575 to 0.559.

If the steam is superheated for the first half of the expansion, and supersaturated for the last half, as in Examples 6 and 7, it is not possible with the empirical formula to represent the curve of constant  $f$  quite so closely with a single value of  $m$  obtained as above described. If  $F = 0.60$ , the value of  $m$  obtained from the final state is 0.1084. The empirical formula for the expansion curve gives  $f$  increasing at first from 0.56 to 0.58, and then diminishing to 0.56. By finding  $m$  for the two parts of the expansion separately, constant values of  $f$  may be obtained for each, but these are necessarily different unless the intermediate or the final value of  $H$  is chosen to make them the same. Thus with  $H_g'' = 687.80$  (dry sat.) in Example 7, we find  $f = 0.567$  (constant) when  $m = 0.1275$  for the superheated stages. To get the same value of  $f$  constant for

\* This is a satisfactory approximation for small ranges of pressure as explained in a previous section (94), and is good for a single stage.

the supersaturated stages, the final value of  $H$  must be 587.8, with  $m = 0.0794$ .

**144. Effect of Speed and Dimensions.** It is of interest to enquire how far results obtained by purely theoretical assumptions with regard to the form of the characteristic curve by the methods illustrated in this chapter, can be realised in practice, and how they may be related to the speed and dimensions of the machine. A consistent method of doing this is afforded by the relation between speed, dimensions, and efficiency, given in § 127, Chapter XI.

The assumption made in the present chapter that the initial velocity  $U'$  of the steam in each stage on leaving the nozzle is the equivalent of the adiabatic heat-drop  $DH_\phi$  in the nozzle, without any deduction for friction or allowance for velocity carried over, may be compared with the assumption made in the previous chapter that the energy of the tangential component  $U' \sin \alpha$  of the effective steam-velocity is a certain fraction  $f'_2$  of the whole energy  $\int aVdP$  available in the stage considered. Comparing the two equations,

$$DH_\phi = U'^2/2Jg, \text{ and } f'_2 \int aVdP = U'^2 \sin^2 \alpha / 2Jg, \dots (16)$$

we observe that, since  $\int aVdP$  must be nearly equal to  $DH_\phi$  for any nozzle, the two assumptions are in good agreement, provided that  $f'_2 = \sin^2 \alpha$ , which gives the value 0.85, if  $\sin \alpha = 0.922$ , or if  $\beta = 22^\circ 47' = 90^\circ - \alpha$ , for the angle which the steam jet makes with the plane of the wheel. Taking this value of the constant for purposes of comparison, it is easy to deduce corresponding values of  $f'$ ,  $f''$ ,  $z$ , and  $u$  for any of the examples taken in this chapter.

Taking Example 1 by way of illustration, in which it was assumed that  $R$  was constant throughout the expansion, or that the characteristic could be represented by a straight line on the  $H\Phi$  diagram—one of the assumptions most frequently made on account of its simplicity—it is instructive to consider three possible cases, (1) that the machine is designed so that the velocity-ratio  $U'/u$  is constant throughout, (2) that  $u$  is constant, (3) that the reaction efficiency  $f''$  is constant.

(1) If  $U'/u$  is constant,  $z$  and  $f'$  are also constant, and  $f'' = f/f'$ . With  $U'/u = 8$ , we obtain the results given in the following table, which show that  $u$  must increase with  $U'$ , and that  $f''$  must diminish in the same ratio as  $f$  throughout the expansion.

Table VI. Variation of  $u$ ,  $z$ ,  $f'$  and  $f''$  in Example 1, § 140.

No.	1	2	3	4	5	6	7	8	9	10
$U'$	1277	1286	1296	1306	1316	1326	1336	1346	1356	1367
$f$	0.600	0.659	0.682	0.574	0.565	0.556	0.548	0.540	0.532	0.524
(1) If $U'/u = 3$ , $z = 2.766$ , $f' = 0.786$ , $f'' = f/0.785$ .										
$u$	426	429	432	435	439	442	445	449	452	456
$f''$	0.765	0.753	0.741	0.732	0.721	0.709	0.699	0.688	0.677	0.667
(2) If $u = \text{const.} = 461$ , $z = U'/500$ , $f'' = 1.149/(z - 1)$ , $f' = f/f''$ .										
$z$	2.554	2.572	2.592	2.612	2.632	2.652	2.672	2.692	2.712	2.734
$f'$	0.813	0.808	0.805	0.804	0.802	0.800	0.798	0.795	0.793	0.791
$f''$	0.739	0.731	0.722	0.713	0.704	0.695	0.687	0.679	0.671	0.663
(3) If $f'' = \text{const.} = 0.800$ , $f' = f/f''$ , $z$ from $f'$ , $u = 0.922U'/z$ .										
$f'$	0.750	0.739	0.727	0.717	0.706	0.695	0.685	0.675	0.665	0.655
$z$	3.04	3.12	3.22	3.31	3.39	3.49	3.57	3.65	3.74	3.83
$u$	387	380	371	364	358	350	345	340	334	329

(2) If the mean blade-velocity  $u$  is the same in different expansions, as is often the case in modern machines,  $f'$  will diminish slightly in consequence of the increase of  $U'$  and  $z$ , but  $f''$  will still diminish excessively.

(8) The assumption  $f''$  constant requires an excessive diminution of  $u$  in the later stages, and this effect would be further exaggerated if allowance were made for the probable increase of  $f''$ . It seems highly improbable that any existing machine could give a characteristic of the type  $F = \text{constant}$ .

The values of  $U'$  and  $f$ , required in the calculation, are taken from § 140, Example 1, and repeated at the head of Table VI to save reference. When  $u$  is given, the value of  $f''$  is deduced from that of  $DH''$ , which is 10.853 for each stage in this example. The value of  $z$  is most easily obtained from  $f'$ , when this is known, by means of a curve, which saves solving the quadratic.

The expression given in Chapter XI, § 127 (21), for the pressure-drop in one expansion of a reaction turbine, does not apply to the case of the impulse turbine because we require the *final* value of  $z$  after expansion through the nozzle, whereas  $z_m$  in (21) is the *mean* value during expansion in the several stages. This relation is replaced by its equivalent  $144MV' = U'X'$ , for the impulse turbine.

If we treat Example 2 in the same way, taking a uniform blade-speed,  $u = 461$  ft./sec., we obtain the following results.

Example 2.  $u = 461, z = U/\sqrt{500}, f'' = 1.149/(z - 1), f_2' = 0.85 = f_2'',$   
 $l'' = 0.176.$

$z$	2.860	2.800	2.744	2.688	2.634	2.580	2.524	2.470	2.420	2.370
$f'$	0.772	0.779	0.786	0.793	0.801	0.809	0.814	0.819	0.824	0.829
$f''$	0.618	0.638	0.659	0.681	0.703	0.727	0.754	0.782	0.809	0.839
$x$	1.5	2.0	2.5	1.0	1.4	2.0	2.8	4.2	6.7	10
$f_x''$	0.610	0.638	0.656	0.681	0.724	0.762	0.787	0.808	0.824	0.832

The values of  $z$  here show a decrease corresponding with the decrease of  $U'$ , and those of  $f'$  a small increase. The values of  $f''$  show an increase as expansion proceeds corresponding closely with those of  $f$  in the original table. These are compared with a formula of the type  $f_x'' = f_2'' - l''/x$ , in which the constant  $f_2''$  is taken as 0.85 in the later stages when peripheral admission is complete, and as 0.726 in the first three stages, when the admission is assumed to be partial. The relative values of the blade-heights given in the line  $x$ , are taken from an existing machine. The resulting values of  $f_x''$  show good general agreement with the values of  $f''$  obtained from the particular type of characteristic assumed in Example 2, except that the rate of variation given by the curve is too nearly uniform throughout, and is more rapid than we should expect in the later stages, where the efficiency should approach a maximum.

In practice, with a turbine of this type, a superheat of at least  $100^\circ$  to  $150^\circ$  F. would be employed, and the efficiency of a large machine would be a good deal higher (about  $F = 0.70$  with superheat) than the value  $F = 0.60$  taken in the example for saturated steam. The variation of  $f$  from stage to stage would be more nearly represented by the curve of Example 7, but unfortunately there are no data available in the published tests for the calculation of the efficiency for the separate stages. Allowing for the effects of supersaturation, the efficiency in the later stages might be appreciably reduced, especially as no allowance for this effect would have been made in the design. But supersaturation would not be nearly so important with initial superheat as with steam initially saturated. The examples in the next chapter are intended to show the general nature of these effects, so far as they can be predicted.

The methods described in the two preceding chapters, depending on the assumption of a particular type of characteristic curve, or of particular constant values of the stage-efficiency, may be applied for rough calculations of the relative dimensions of a machine, or of the pressure-distribution corresponding to the assumptions

made. Conversely, in experimental tests, when the dimensions and speed are known, and the pressure-distribution is observed, if the actual form of the characteristic can be determined from the tests, or assumed from previous experiments on similar machines, it is possible to deduce the efficiency in the separate stages, and to estimate the effect of any improvements made in the design.

In using the  $H \log P$  diagram, the efficiency at any point of the curve may be determined by drawing a tangent and measuring the slope  $\tan \theta$  from the ratio of the vertical and horizontal intercepts in millimetres. The value of the stage-efficiency  $f$  is deduced from the observed slope on the actual scale of the diagram by the numerical formula,

$$f = 528 \tan \theta / PV \dots \dots \dots (17)$$

if the product  $PV$  is taken at the required point in F.P.C. or F.P.F. units.

It is very often assumed that the efficiency of each separate stage, or the relative efficiency of the whole, will remain constant under different conditions of load, or vacuum, or superheat; but this assumption appears to give results materially at variance with experiment, as shown later. The reason is that any variation in the conditions of running will entail corresponding variations in the velocity-ratio, which affects the efficiency of the separate stages in the manner shown by the curves in Fig. 29. The object of the formulae explained in § 127 is to meet this difficulty by taking account of the variation of the kinetic efficiency  $f'$ , with variation of the velocity-ratio  $z$ . The efficiency constant  $f'_0$ , and the reaction efficiency  $f''$ , may be assumed to remain constant for each stage under various conditions, and the equations then permit the calculation of the appropriate values of  $z$ ,  $DH$ ,  $DP$ , and  $f$ , for the various stages. The method of calculation is illustrated by the following example.

*Example 8.* Taking the data of Example 5, with equal division of work and available energy between the stages, find how the distribution of pressure will be altered, at  $u = 500$  ft./sec., if  $M$  is reduced to  $1/2$  by cutting out some of the first set of nozzles, the other conditions remaining unaltered.

In finding the effect of change of conditions, it is frequently permissible to introduce simplifications, provided that both parts

of the calculation are made in the same way. The steam being dry, we may neglect  $b$ , and take  $DaPV = 8DH/18 = 3.280$  for each stage. The available energy,  $\int aVdP$  for each stage is 25.87 cal. C. The index  $m$  in the expansion curve  $PV = kP^m$  is constant and equal to  $3.28/25.87$ . The values of  $aPV$  form an arithmetical progression, from which the values of  $P$  at intermediate points are readily deduced by logarithmic interpolation, as in Chapter XII, Example 3, by the formula,

$$m \times \log (P'/P'') = \log (P'V'/P''V'').$$

The values of  $P$  thus obtained at the intermediate points are shown in the following table, and do not differ materially from those previously given in Example 5, though obtained by a much simpler method on slightly different assumptions.

Table VIII. Pressure Distribution for Normal Conditions.

Point No.	1	2	3	4	5	6	7	8	9
$aPV$	64.35	61.12	57.89	54.66	51.43	48.20	44.97	41.74	38.51
$P$	112.3	75.00	49.00	31.20	19.34	11.61	6.727	3.758	1.994
$100z/V''$	50.03	35.17	24.26	16.36	10.78	6.906	4.288	2.582	1.484

For simplicity, the stage-efficiency  $f$  is preferably defined as the ratio of  $DH$  to the whole available energy in each stage, in place of the adiabatic heat-drop in the nozzle. This gives

$$f = 14/25.87 = 0.552 \text{ (constant).}$$

If  $f_2' = 0.85$ , as in (16), in the equations,

$$\int aVdP = z^2 u^3 / 2Jg f_2', \text{ and } DH = 4(z-1)u^2 f'' / 2Jg, \dots (18)$$

we must have  $z = 2.788$ ,  $f'' = 0.706$ , both constant under normal conditions. In general,  $f''$  would increase in the later stages, but the assumption,  $f = \text{constant}$ , is so commonly made that it may be adopted for simplicity in the calculation, since the variation of  $f''$  is immaterial for the present purpose.

The value of  $z$  in any stage follows from the definition (§ 114),

$$z = U \tan \alpha / u = U' \sin \alpha / u = 144MV' \sin \alpha / uX', \dots (19)$$

from which it appears that  $z/V''$  will vary nearly in the same way as  $M$  when  $\alpha$ ,  $u$ , and  $X'$  remain constant, as in the present example. Thus the final value of  $aPV$  for stage 10 at 1 lb. being 85.28, the final value of  $V''$  is 848.0, and the ratio  $z/V'' = 2.788/848 = 0.00318$ , under normal conditions. When  $M$  is reduced to  $1/2$ , the value of

$z/V''$  for this stage will be reduced to 0.004065, and similarly for the other stages, for which the normal values of  $z/V''$  are given in Table VIII.

To find the intermediate pressures when  $M$  is reduced to  $1/2$  since  $m$  will no longer be constant, it is most convenient to start with an assumed value of the final volume, and calculate the stages in succession. With the above value of  $z/V''$  for the last stage, if  $V'' = 852$ , we have  $z = 1.481$ . To find  $DH$ ,  $DaPV$ , and  $DP$ , we have from (18) the simple numerical formulae,

$$DP = P'' / (0.3064 a P_m V_m / z^2 - 1/2),$$

and

$$DH = 7.88 (z - 1) = 18 DaPV / 3, \dots\dots\dots (20)$$

in which the approximate expression  $a P_m V_m DP / (P'' + DP/2)$  is taken for  $\int a V dP$ , which, as previously explained in § 107, is near enough, provided that  $DP$  is not greater than  $P''/2$ . Thus we find, for the last stage, with  $P'' = 1$  lb.,  $DH = 3.88$ ,  $DaPV = 0.78$ ,  $a P'' V'' = 86.40$ ,  $a P_m V_m = 86.79$ ,  $DP = 0.260$ ,  $P' = 1.200$ . From  $a P' V' = 87.18$ , we find  $V' = 801.8$ , giving  $z = 2.236$  for the next stage. Since we are concerned chiefly with small differences, all the operations may be very quickly and easily performed with a small slide-rule. The value of  $z$  comes out nearly constant for the next seven stages, varying only from 2.67 to 2.68. Except for the last two stages, the values of  $P$  are all about 2 per cent. less than half the values in Table VIII. The pressure in the first chamber comes out 54.6 lbs., giving a drop of 110 lbs. for the first nozzles. By hypothesis  $X$  is changed for these nozzles, so that  $z$  cannot be deduced from  $V''$ , but must be calculated from (18) using the logarithmic formula for  $\int a V dP$ , with the given value of  $DP$ . This will give fairly probable values of  $z$  and  $DH$ , assuming that the nozzle is designed to suit so large a range of pressure-drop. A nozzle with a long and nearly uniform throat, as shown by the curve  $X_u$  in Fig. 24, would be suitable for a considerable range, but more details would be required for an exact calculation.

Owing to the diminution of pressure at  $M = M_0/2$ , there is an appreciable reduction of available energy and heat-drop in the last nine stages, but the efficiency of these stages is slightly improved owing to the reduction of  $z$ . The heat-drop in the first stage is doubled, but the efficiency is reduced to  $f = 0.405$ . The total heat-drop, under the conditions assumed, is reduced from 140 at  $M = M_0$  to 134 at  $M = M_0/2$ .

It is often desirable in the case of turbo-electric generators to



maintain a high efficiency at low loads, with a maximum somewhere between  $1/2$  and  $3/4$  load, as shown by the lower curve in Fig. 28. One of the simplest ways of doing this, in the present example, would be to replace the first wheel by a compound wheel. This would involve a slight reduction of efficiency in the first stage at full load, assuming that the steam-velocity remained the same, but the efficiency would improve with increase of steam-velocity, reaching a maximum in the neighbourhood of  $z = 4$ , and maintaining a high value at low loads, when the heat-drop in the first stage is a large proportion of the whole, according to the method of regulation by cutting out nozzles.

The reason why a reciprocating engine, when regulated by varying the cut-off, gives a curve of a similar type, with a maximum efficiency at intermediate loads, is that, beyond a certain point, the increase of cylinder condensation and leakage more than counterbalances the improvement due to increase of expansion-ratio.

*Regulation by Throttling.* When the regulation is effected by throttling the initial pressure in place of cutting out nozzles, the same method of calculation applies. If the same final state is assumed, the numerical results will be the same for the last nine stages, and the pressure-drop for the first stage may be calculated in the same way as for the other stages. With a final volume,  $V'' = 852$ , as above, the initial pressure comes out 80.4 lbs., but the initial value of  $H$  is only 738.8 in place of 756. If the initial value of  $H$  is supposed to remain constant and equal to 756 when  $M$  is reduced to  $M_0/2$  by throttling, we require a final volume  $V'' = 874$ , and the initial pressure is found to be 82.9 lbs., or very nearly half that at full load.

It appears, according to this method of calculation, that the flow  $M$  is very nearly proportional to the initial pressure when the regulation is effected by throttling at constant  $H$ . This is closely confirmed by experiment, and may generally be assumed in making the calculation in the opposite order, starting with the initial state, for any given fraction of the normal mass-flow.

The heat-drop becomes *negative* for values of  $z$  less than unity in the later stages at low loads. Work is wasted in friction, giving an increase in place of a diminution of  $H$ , apart from external heat-loss. The following table shows the effect in question, which begins to appear in the neighbourhood of quarter load in the present example.

Table IX. Regulation by Throttling.  $M = M_0/4$ .

No.	1	2	3	4	5	6	7	8	9	10
	2.783	2.761	2.760	2.759	2.758	2.757	2.665	2.184	1.445	0.840
$DH$	13.80	13.79	13.78	13.78	13.77	13.76	13.04	9.27	3.48	-1.25
$V$	41.43	28.22	18.88	12.33	7.872	4.683	2.936	1.769	1.239	1.056

$P'$  is the initial value of  $P$  in each stage. The initial value of  $H$  is taken as 756, and the final value of  $V''$  is 414 cb. ft. at 1 lb. The total heat-drop is 107.2. The same equations (20) are employed throughout for  $DP$  and  $DH$ , but the values of  $z/V''$  are  $1/4$  of those given in Table VIII. If the regulation is effected by cutting out nozzles in place of throttling, the calculation is the same, except for the first stage, but the final volume is 380, and the total heat-drop may be as high as 124 nearly, if full efficiency is assumed for the first nozzles in spite of the excessive pressure-drop.

The cut-out method will always give better efficiency than simple throttling at low loads, because it utilises the full pressure-drop. For this reason among others, the first stages of a reaction turbine are often replaced by impulse-wheels. The effects obtained in the early stages depend greatly on details of design, but the two types are essentially similar in the later stages, so that similar methods apply. Many of the results obtained for reaction turbines in the two following chapters apply with slight modifications to impulse turbines.

## CHAPTER XIV

### REACTION TURBINE ANALYSIS

#### 145. Calculation of the Flow Through an Expansion.

The equations given in Chapter XI, § 127, for the flow through an expansion consisting of  $N$  similar pairs of fixed and moving blades with the same annular area  $X$ , can be applied to the solution of any thermodynamical problem relating to the flow through a reaction turbine when sufficient data are available.

The equations in question may be summarised as follows:

$$\text{Available energy, } \int aVdP = (Nu^2/Jg) z_m^2/f_1' = Zz_m^2/f_1', \dots(1)$$

$$\text{Heat-drop, } DH = H' - H'' = (2z_m - 1) f''Z, \dots\dots\dots(2)$$

$$\text{Pressure-drop, } DP = P' - P'' = NuMz_m \tan \alpha/gf_1'X, \dots\dots(8)$$

where  $z_m$  denotes the mean effective value of the velocity ratio  $z = U \tan \alpha/u$ , and  $Z$  is used as a convenient abbreviation for the energy constant  $Nu^2/Jg$  of the expansion considered. The method of applying these equations depends on the object of the investigation and on the available data. It will be convenient to distinguish three general cases among many possible varieties.

(1) *Efficiency Tests.* When the dimensions are known, and the heat-drop, pressure-drop, mass-flow, and speed are observed, the equations can be employed for finding the efficiency constants  $f_1'$ ,  $f''$ , and the velocity ratio  $z_m$ .

(2) *Variation of Conditions.* When the efficiency constants are known from tests under standard conditions, the equations may be employed for investigating the effect of variation of conditions of running, or state of the steam, such as (a) Speed, (b) Initial or Final Pressure, (c) Superheat, Wetness, or Supersaturation.

(8) *Choice of Dimensions.* When the constants are known from tests of similar machines, the equations can be employed for choosing suitable dimensions for any desired purpose, having regard to the limitations of speed and pressure-range, and to the probable state of the steam.

It is proposed in the present chapter to give examples of different methods of solution in various cases, and to discuss the limits

within which the equations may legitimately be applied, either to a single expansion, or to a complete turbine.

*Dimensional Constants.* For thermodynamical purposes, the material dimensions of an expansion can be summarised by two constants, which, with the speed  $R$  in revs./min., suffice to define the properties of the expansion, independently of the absolute dimensions in many respects.

*The Energy Constant,  $Z = Nu^2/Jg$ ,* in thermal units (cals. C., or B.Th.U.), enters into the expressions for the available energy and the heat-drop.  $Z$  varies as the square of the speed, but since all the values of  $Z$  for the expansions on any one rotor are changed in the same proportion when the speed is varied, it is most convenient to include the speed in  $Z$  by calculating the values for normal speed, and reducing them by a constant factor, proportional to  $R^2$ , when the speed is changed.

*The Expansion Constant,  $Z' = Nu \tan \alpha / X = NR \tan \alpha / 720x$ ,* determines the pressure-drop  $DP$  in conjunction with  $M$  and  $z_m$ , and incidentally the appropriate expansion-ratio. If  $M$  and  $z_m$  are the same for the different expansions on one rotor under normal conditions of running, the values of  $DP$  will be simply proportional to those of  $Z'$ , a condition which is readily tested at any time.

*The Discharge Constant,  $Z'' = aZ'^2/gZ = 144N \tan^2 \alpha / X^2$ ,* is not an independent constant, since it can be deduced from  $Z$  and  $Z'$ , but is useful in calculating the discharge  $M$ .  $Z''$  has the advantage of being independent of the speed, and is useful for finding the pressure-distribution, as explained in the next chapter, when  $M$  is the same, but  $z_m$  different, for the different expansions in a turbine.

The effects of *tip-leakage*, as explained in the next chapter, are of considerable importance in modifying the flow and the efficiency in a high-pressure turbine, because they affect the different expansions in different degrees. Fortunately the expansion constant  $Z'$ , and the discharge constant  $Z''$ , are readily corrected for tip-leakage by simply substituting  $x + 2l$  for  $x$ , where  $l$  is the tip-clearance. This correction does not affect the relative values for a single expansion, and will therefore be omitted in the present chapter, since it may be supposed to be included in the given values of the constants  $f''$  and  $x$ .

As an example we may take the first expansion of a large slow-speed marine turbine (SS. *Mauretania*) with the following dimensions:

Rotor diameter, 96 in., cylinder, 101.5 in., area,  $X = 858$  sq. in.  
 Number of stages,  $N = 16$ , discharge angle,  $\alpha = 70^\circ$ ,  $\tan \alpha = 2.7475$ .  
 At 194 revs./min.,  $u = 88.6$  ft./sec.,  $Nu^2/Jg_c = Z = 2.480$  cal. C.

We will first find the values of  $f_1'$ ,  $f''$ , and  $z_m$  for the following conditions, which correspond closely with the normal conditions of running:

Initial pressure, 150 lbs. (gauge), final, 115 lbs., bar. 80 in.

Mass-flow,  $M = 116$  lbs./sec., heat-drop,  $DH = 6.28$  cal. C.

which give the following values of  $P$ ,  $V$ , and  $H$ :

Initial state (dry sat.),  $P' = 164.7$ ,  $H' = 667.54$ ,  $V' = 2.785$  (F.P.C.)

Final state (supersat.),  $P'' = 129.7$ ,  $H'' = 661.26$ ,  $V'' = 3.424$  „

Substituting the given data in equation (8), we find

$$z_m/f_1' = DP_g X / Nu M \tan \alpha = 2.255.$$

Putting this value in equation (1) with  $\int aVdP = 11.09$ , we find

$$z_m = 11.09 / 2.255 \times 2.480 = 1.988,$$

whence

$$f_1' = 0.880, \quad f' = 0.664.$$

Finally from equation (2), we obtain  $f'' = 0.854$ ,  $f = 0.566$ .

When all the required data are given, the calculation of the constants is very simple, but there are some points which require discussion.

**146. The Available Energy.** The value of  $\int aVdP$  in equation (1) may be taken roughly as  $aP'V' (P' - P'') 2/(P' + P'')$ , when  $V''$  is unknown, but this is insufficiently accurate for large ranges of pressure. It gives 11.22 cal. in the present case, which is a fair approximation, because the pressure range is small, but it is better to use the formula,

$$\begin{aligned} \int aVdP &= (aP'V' - aP''V'') \log (P'/P'') / \log (P'V'/P''V'') \\ &= D (aPV)/m, \dots\dots(4) \end{aligned}$$

as explained in Chapter X, § 107, which gives very accurate results for the available energy, even if the value of  $V''$  is only approximate, or if the actual expansion curve does not agree very closely with the formula  $PV = kP^m$ . Any small error in the difference  $P'V' - P''V''$  is compensated by the corresponding error in the difference between the logarithms of the same numbers, and does not give rise to a proportionate error in the value found for the integral. The ratio of the difference of the logarithms of  $PV$  to that of the logs of  $P'$  and  $P''$  gives the value of the index  $m$  in the formula  $PV = kP^m$ , which is often required. If the heat-drop  $DH$  is varied

in the present case over the extreme range from zero to the adiabatic value 10.96, the available energy varies only from 11.265 to the same adiabatic value, a variation of less than 8 per cent., so that it is not necessary to know  $DH$  very accurately in order to get a good value of  $z_m$  from equation (1).

The formula for the integral of  $aVdP$  takes no account of possible variations in the form of the expansion curve between the initial and final states, but this makes very little difference to the value of the integral (especially for small ranges of pressure), as is most easily appreciated by taking a numerical example. For given initial and final values of  $P$  and  $V$ , the form of the expansion curve can be represented very closely in all practical cases by an equation of the type  $H - B'' = kP^m$ . The integral of  $aVdP$  along a curve of this type in the case of dry steam is accurately given by

$$\int aVdP = (8/13) (B'' - 464) \log_e (P'/P'') + 3DH/13m + 0.00127 DP, \dots (5)$$

which is easily calculated. With the initial and final states above given, the expansion curves differ quite appreciably for the two cases,

$$(1) z = 1.983 \text{ (constant), } \alpha_m = 70^\circ,$$

and

$$(2) \alpha = 70^\circ \text{ (constant), } z_m = 1.983.$$

The corresponding values of the constants in the formula

$$H - B'' = kP^m$$

are:

$$(1) B'' = B = 464, m = 0.18120,$$

$$(2) B'' = 627.26, m = 0.7095,$$

which are widely different; but the values of the integral of  $aVdP$  along either curve are very nearly the same, namely, (1) 11.089, (2) 11.087. The fact that the available energy varies so little under different conditions when the initial and final states are given, makes equation (1) a very convenient and consistent method of calculating the mean effective value of  $z$  in any case.

**147. The Velocity-Ratio  $z$ .** The usual method of calculating the value of the velocity-ratio in each expansion for normal blades is to take the effective aperture of the guide-blades as one-third of the annular area  $X$ , which gives

$$U'/u = 482MV/\mu X = U \sec \alpha/u,$$

which is not quite the same as  $z$ . This is equivalent to taking the

discharge angle  $\alpha$  as  $70^\circ 32'$ , but the fraction of the degree above  $70^\circ$  is unimportant for the present purpose.

The value of  $\alpha$  required in the formula for  $z$ , namely,

$$z = 144MV \tan \alpha / uX, \quad \dots\dots\dots(6)$$

is the angle which the direction of the discharge makes with that of the axis, in the clearance space between the blades. This cannot be measured with great precision, but may be assumed to remain *constant* for any particular blade-ring when any of the other conditions are changed, and to remain *uniform* throughout the expansion if the blade-angle is uniform. The blade-angle may be varied in different ways, but it will suffice for the present purpose to consider only two cases, (1) that in which the blade-angle is varied in such a way as to keep  $z$  the same for each step in the expansion, (2) that in which the discharge angle is the same for each step.

(1) If  $z$  is to be uniform, it is evident from (6) that the product  $V \tan \alpha$  must be the same for each blade-ring at exit; and it follows from (1) and (8) that the common value of the product must be  $V_m' \tan \alpha_m$ , where  $V_m'$  is the mean value of  $V$  at equal intervals of  $P$ , given by  $V_m' DP = \int V dP$ , and  $\tan \alpha_m$  is the value of  $\tan \alpha$  employed in equation (8). The method of solution previously given will be *exact* in this case, which is of theoretical interest on account of its simplicity, but is seldom adopted in practice.

(2) If the blade-angle is uniform throughout the expansion, it is evident from (6) that  $z$  must vary directly as  $V$ , and from (1) that the pressure-drop in each step will also be nearly proportional to  $V$ . It follows that the drop of  $P/V$  will be nearly the same in each step, and that the mean values of  $V$  and  $z$  for the expansion must be taken at equal intervals of  $P/V$ . The required mean value of  $V$  along the curve  $PV = kP^m$ , is given by the formula,

$$V_m'' = (2 - m) (P' - P'') / (P'/V' - P''/V'') = (2 - m) DP / D(P/V). \quad \dots\dots(7)$$

The mean value of  $\tan \alpha$ , if required in case (1), may similarly be found by taking the mean value of  $1/V$  at equal intervals of  $PV$ ,

$$(1/V)_m = DP / \int V dP = 144M (\tan \alpha)_m / z_1 uX, \quad \dots\dots(8)$$

which is seen to be simply the reciprocal of  $V_m' = \int V dP / DP$ , as stated above.

Owing to the difference between  $V_m''$  and  $V_m'$  there will be slight differences between case (1) and case (2), which will be

discussed in detail in a later section, but the correction required for case (2) in the previous example would be only 1 in 300 on  $DH$  or  $M$ , and is seldom of much importance in any practical case.

• 148. **Correction for Discontinuity of Expansion.** It might naturally be expected that the employment of methods of continuous integration would give rise to material discrepancies in the calculation, since the expansion is really discontinuous, taking place in  $2N$  separate steps. It follows however from the form of the equations that this will not introduce any material errors in the proposed method of calculating  $z_m$  or  $DH$ , but it may be necessary in exceptional cases to apply a correction for discontinuity to the value found for  $M$  in case (2). It happens however that the correction is of the opposite sign to that discussed in the previous section, and is nearly of the same order of magnitude, so that both may be neglected in the majority of practical cases, so far as  $M$  is concerned, unless the object is to test the limit of accuracy of the method of calculation.

The value of  $V_m''$  given by the continuous integral in (7) is very nearly the mean of the values of  $V$  at the *middle points* of the separate steps, but differs slightly from the mean of the values of  $V$  at the *ends* of the steps, which is the mean required for deducing  $M$  from  $z_m''$  by equation (6). If  $V_0$  is the initial value of  $V$ , and if  $V_1, V_2, \dots, V_{2N}$ , are the final values of  $V$  in each step, it is evident that the value of  $V_m''$  given by (7) satisfies the formula

$$2NV_m'' = V_0/2 + V_1 + V_2 + \dots + V_{2N-1} + V_{2N}/2,$$

since the mean value of  $V$  for each step is very nearly the mean of the initial and final values when the steps are small. Thus the correction to be added to  $V_m''$  in order to obtain the mean of the values from  $V_1$  to  $V_{2N}$ , excluding  $V_0$  but including  $V_{2N}$ , is evidently  $(V_{2N} - V_0)/4N$ , which may conveniently be written  $DV/4N$ , where  $DV$  is the difference of the initial and final volumes for the whole expansion. This correction has the effect of *reducing*  $M$  in case (2) by the fraction  $DV/4NV_m''$ , which amounts to 1 in 300 in the previous numerical example. The correction discussed in the preceding section has the effect of *increasing*  $M$  in case (2) by half the percentage difference between  $V_m'$  and  $V_m''$ . Both corrections increase with the expansion-ratio, but they become equal and opposite when  $V_m' - V_m''$  is equal to  $DV/2N$ , which would happen in the previous example if the expansion-ratio were nearly doubled.



It follows that both corrections may usually be neglected for practical purposes through a fairly wide range.

**149. The Efficiency-Constant  $f_1'$ .** The preceding comparison between the two cases, (1)  $z$  constant, and (2)  $\alpha$  constant, rests on the assumption that the coefficient  $f_1'$  is independent of the discharge angle  $\alpha$ , which cannot be *exactly* true. It is probable, however, that there is a maximum value of  $f_1'$  somewhere in the neighbourhood of  $\alpha = 70^\circ$ , so that  $f$  may be taken as constant when  $z$  is constant for a moderate range of variation of  $\alpha$ . It is evident that for very fine angles of discharge ( $\alpha$  near  $90^\circ$ ), the losses due to the axial clearance, to the thickness of the blades, and to the curvature of the blade-path, must increase considerably. On the other hand, when the blades are opened out ( $\alpha$  diminished), the value of  $f_1'$  tends to diminish, because the tangential or *effective* component of the velocity is reduced in comparison with the whole velocity on which the frictional losses chiefly depend. We may safely assume that the angles adopted in practice represent an empirical compromise between these conflicting interests, and give a fair approximation to the condition of maximum efficiency. The published data do not afford sufficient evidence for the proper investigation of this point, but it seems fair to assume the approximate constancy of  $f_1'$  in the case of normal blades. In the case of wing-blades, when the reduction of  $\alpha$  is pushed to extremes, there will doubtless be an appreciable reduction of efficiency, which appears to require further investigation.

In finding the value of  $f_1'$  from experimental observations, it will be seen that an error of 1 per cent. either in the observed value of  $M$ , or in the assumed value of  $\alpha$ , will introduce an error of 2 per cent. in the resulting value of  $f_1'$ . It may for this reason be preferable, if the values either of  $M$ , or of  $\alpha$ , are uncertain, as is sometimes the case, to employ the equation with an assumed value of  $f_1'$  for deducing either  $M$  or  $\alpha$ , or the product  $M \tan \alpha$ , if both are uncertain. It is often possible to obtain reliable results with regard to the variation of other conditions, without an exact knowledge of the absolute values of  $f_1'$ ,  $M$ , and  $\alpha$ , provided that the conditions are such that these quantities can be regarded as constant. Even when the observations are incomplete in certain respects, it does not necessarily follow that they are useless for the purposes of analysis. Unless otherwise stated the value 0.888 will usually be taken for  $f_1'$  in a slow-speed marine turbine.

**150. To Find the Final State given  $f_1'$  and  $f''$ .** When the efficiency constants are given, in addition to the dimensions, speed, and initial state, the final state, required for the beginning of the next expansion, can be found with the aid of any one of the remaining unknown quantities, namely,  $\int aVdP$ , or  $z_m$ , or  $DH$ , or  $DP$ , or  $M$ , or  $f$ , or  $f'$ . The quantity most readily observed is  $P''$ , giving  $DP$ ; but in many cases  $M$  only is given, and is subject to uncertainties of dummy-leakage, though it may remain constant for several successive expansions. In the case of superheated steam,  $H''$  or  $DH$  may be observed in addition to  $P''$  by observing the temperature, but  $DH$  or  $\int aVdP$  generally occur as data in the inverse problem of finding the dimensions to suit equal division of the heat-drop or available energy. The simplest case is that in which  $z_m$  is given, which readily permits direct solution of the equations in the case of dry steam. If  $\int aVdP$ ,  $DH$ ,  $f$ , or  $f'$  is given,  $z_m$  is easily found, but, in the case of saturated steam, it is necessary to proceed by trial and interpolation, with the aid of the tables.

Taking the dimensions and speed given in the previous example, with the values  $f_1' = 0.880$ , and  $f'' = 0.842$ , the three equations reduce immediately to the following numerical forms:

$$\begin{aligned}\int aVdP &= 2.818z_m^2 \dots (1), & DH &= 2.088 (2z_m - 1) \dots (2), \\ DP &= 0.1520Mz_m \dots (3).\end{aligned}$$

If  $z_m$  is given,  $DH$ ,  $f$ ,  $f'$ , are easily found.  $P''$ , and hence  $DP$  and  $M$ , are obtained by inverting the formula for  $\int aVdP$ , thus,

$$\log (P'/P'') = 2.818z_m^2 \log (P'V'/P''V'') / (aP'V' - aP''V'').$$

In the case of dry steam, the drop of  $aPV$  is given in (F.P.C.) units by the exact formula,

$$DaPV = aP'V' - aP''V'' = 3DH/18 + 0.00127DP, \dots (9)$$

in which the last term may usually be neglected.

In the present example, suppose that it is required to find  $DP$  for the case in which  $z_m = 2$ , with the initial state  $P' = 164.7$ ,  $aP'V' = 47.17$ . From (2),  $DH = 6.624$ , whence  $DaPV = 1.445$ , if  $0.00127DP$  is neglected.

$$\begin{aligned}\log (P'/P'') &= 11.272 \times 0.018512 / 1.445 = 0.10540, \\ P'' &= 129.21, \quad M = 116.7.\end{aligned}$$

If the small term is *not* neglected,  $DaPV = 1.490$ ,  $P'' = 129.19$ ,  $M = 116.8$ . The small change in  $DaPV$ , changes  $\log (P'V'/P''V'')$  to 0.018940, in nearly the same proportion as  $DaPV$ , so that the result is very little altered.

If  $DP = 85.51$  is given in place of  $z_m = 2$ , we have first to find an approximate value of  $z_m$  from the formula

$$\int aVdP = aP'V'2DP/(P' + P_c^h),$$

which gives  $\int aVdP = 11.40$ ,  $z_m = 2.011$ , in the present case. From which we find,  $DH = 6.81$ ,  $DaPV = 1.500$ ,  $\int aVdP = 11.272$ ,  $z_m = 2.000$ ,  $DH = 6.264$ ,  $M = 116.8$ . The approximation is so rapid that it is seldom necessary to go further.

On the other hand, if  $M = 116.8$  were given in place of  $DP$ , it would be necessary to solve a quadratic in  $z_m$  in order to find an approximate value. It is easier in this case to guess a pair of trial values of  $DP$  and  $z_m$  to fit equation (8), and to use the trial value of  $z$  to find  $DH$  and  $DaPV$  from (2), and the corresponding value of  $DP$  to find  $\int aVdP$  and  $z_m$  from (1). If the first trial values were  $DP = 85$ ,  $z_m = 1.971$ , we should find from (2)  $DaPV = 1.462$ , giving  $\int aVdP = 11.092$ ,  $z_m = 1.984$ , from (1), showing that higher values of  $z$  and  $DP$  are required. The trial value of  $z$  must be raised by rather more than twice the difference between 1.984 and 1.971, suggesting  $z = 2.00$  for the next approximation. If the second trial should not give exact agreement between the values of  $aVdP$  from (1) and (2), the correct result is easily found by interpolation. But by using the more exact rule given in a later section (§ 158), the first trial gives so close an indication of the final result that it is rarely necessary to make a second trial except as a verification.

**151. Effect of the State of the Steam.** The state of the steam is taken into account in the equations in deducing  $V''$  from  $H''$ , or  $DaPV$  from  $DH$ . The steam is usually dry (superheated or supersaturated) in the early stages, which greatly simplifies the work. If the state of saturated steam is assumed in place of dry supersaturated, it makes little difference to the results in the first expansion, starting with dry saturated steam, because the curves have a common tangent at the starting point, and the volumes diverge slowly at first. But in the later expansions the difference may be considerable, as already indicated, and appears to afford a rational explanation of effects which have hitherto been regarded as anomalous. The calculation for saturated steam is made in the same way as for dry steam, except that  $V''$  must be found from  $H''$  in order to find  $DaPV$ , and similarly for the supersaturation limit as previously illustrated in Chapter X.

As a numerical example of the effect of the state of the steam,

we may take the same expansion, with the speed and dimensions already given, but assuming that the initial state of the steam, instead of being dry-saturated, corresponds to a value  $H' = 618.73$  at 160 lbs. abs., which makes the wetness 10 per cent. if the steam is saturated, and gives the value of  $H'$  corresponding to the super-saturation limit, if the steam is dry. Such cases probably occur in actual practice, as a rule at lower pressures and higher speeds, but the general effect of the assumption with regard to the state of the steam is the same, being independent of the particular speed and dimensions assumed. The initial values are:

For saturated steam,  $V' = 2.576$ ,  $aP'V' = 42.39$  (10 per cent. wet).

For supersaturated steam,  $V' = 2.182$ ,  $aP'V' = 35.91$  (dry).

The numerical values of the coefficients in the three equations are the same as those given in the last section. If we take the final pressure 120 lbs. in both cases for convenience of calculation, the first rough approximations to the values of the final volume  $V''$  in either case from equation (1) are:

Saturated,  $\int aVdP = 12.11$ ,  $z = 2.073$ ,  $DH = 6.57$ ,  $V'' = 3.857$ ,  $aP''V'' = 41.43$ .

SS limit,  $\int aVdP = 10.26$ ,  $z = 1.908$ ,  $DH = 5.88$ ,  $V'' = 2.883$ ,  $aP''V'' = 35.58$ .

From which the following final results are obtained by (4),

Saturated,  $\int aVdP = 12.056$ ,  $z = 2.068$ ,  $DH = 6.547$ ,  $M = 127.2$ ,  $f = 0.543$ .

SS limit,  $\int aVdP = 10.282$ ,  $z = 1.910$ ,  $DH = 5.887$ ,  $M = 137.8$ ,  $f = 0.573$ .

The first approximation is so little trouble, and agrees so closely with the second, that it is seldom worth while to go further than the first when the exact state of the steam is uncertain. It will be observed that the flow  $M$  for the same pressure-drop is 8.4 per cent. larger at the SS limit than at the saturation limit, but the steam-speed is also lower by 7.6 per cent., so that the efficiency  $f$  comes out appreciably *higher* when reckoned in terms of the actual energy available at the SS limit, which is nearly 15 per cent. smaller than at saturation. But the *apparent* efficiency at the SS limit, reckoned in terms of the energy theoretically available at the usual saturation limit, is only 0.488, showing an apparent drop of 10 per cent. in efficiency due to supersaturation. The loss would be larger if allowance were not made for the reduction of steam-speed.

In order to detect the difference between saturated steam and dry supersaturated in the first expansion when the initial volumes are the same, it is necessary to take the second approximation to  $aVdP$ , since the first approximation, being simply  $2aPV''/7$  in the present instance, takes no account of the difference between the final volumes. The first approximation to  $z$  is also the same for both, but gives a value of the heat-drop,  $DH = 7.04$ , which is of ample accuracy to determine the appropriate value of the small difference  $DaPV$  in either case. It will be seen from the table below that the values of  $DaPV$  are appreciably different. That for dry steam is very easily found from  $DH$  by formula (9) given in the last section with a small slide-rule, but in the case of saturated steam it is necessary to find  $V''$  from  $H''$  with the aid of the tables, and to use a Fuller slide-rule, or five-figure logarithms, for finding the product  $aP''V''$ .

In order to illustrate the effect of superheat, values are added for the same pressure-range, dimensions, and speed, with initial temperatures of  $200^\circ$ ,  $250^\circ$ , and  $300^\circ$  C. These show an appreciable reduction of  $f$  with superheat due to the increase of steam-speed, and support the view given in Chapter XII, § 187, that the effect of superheat for a given machine at a constant speed cannot fairly be deduced by the method of the reheat-factor assuming that  $f$  remains constant. In order to keep  $f$  constant, it would be necessary to increase the blade-speed in proportion to the steam-speed, which might often be impracticable.

Table I. Effect of Superheat at given speed and dimensions.

$t^\circ$ C.	$V'$	$2aPV/7$	$z_m$	$DaPV$	$aVdP$	$z_m$	$M$	$DH$	$f$
184.16	2.862	13.46	2.165	1.14	13.383	2.179	120.8	7.011	0.524
184.16	2.862	(Dry supersat.)	1.68	13.303	2.173	121.1	6.986	0.525	
200	2.991	14.06	2.233	1.73	13.908	2.222	118.4	7.10	0.517
250	3.386	15.89	2.374	1.86	15.732	2.363	111.4	7.78	0.495
300	3.750	17.63	2.501	1.98	17.466	2.490	105.7	8.31	0.476

The above results are for the same pressure-range, 160–120 lbs. abs., as the last. In a complete turbine, the pressure distribution will vary with superheat, and is determined by calculating the pressure-drop for each expansion in succession with the same value of  $M$  for each, if  $M$  is the same throughout.

**152. Variation of Speed.** It follows from equation (1) at the beginning of the chapter, that the steam-speed depends chiefly on the available energy, and is nearly independent of the blade-

speed, provided that the dimensions remain the same. This result is by no means obvious, apart from the assumptions made, and it is easy to imagine cases in which it would be very far from true; but it appears to accord well with practical experience in the case of reaction turbines, though it is difficult to make a direct test over a wide range on account of other limitations.

In the case of a complete turbine, variation of speed will usually produce secondary variations of pressure in some of the expansions. We will therefore take first the simpler case of a single expansion in which the initial and final pressures are assumed to remain constant when the blade-speed is varied. Taking the same dimensions and pressure-range as in the last example, with the initial state dry sat. at 160 lbs., the values found, at  $u = 88.6$ , were  $z = 2.178$ ,  $M = 121.1$ ,  $DH = 6.986$ ,  $f = 0.525$ . If the speed is changed, the available energy, in the case of dry steam, varies only from 18.54 at  $u = 0$ , when  $DH = 0$ , and  $M = 120$ , to a minimum 18.21 at  $z = 1$ ,  $u = 181.1$ , at which point the heat-drop and mass-flow have their maximum values  $DH = 9.80$ , and  $M = 121.5$ , with  $f = 0.742$ . Further increase of speed to  $z = 1/2$  gives again  $DH = 0$ , with  $u = 366$ ,  $M = 120$ . But this is far beyond the practical range. These equations neglect the effect of fan-action, which varies as the cube of the speed. According to the estimate made in Chapter XI, § 129, the loss due to this cause would amount to about 2 per cent. of the available energy at  $z = 1$ , or about 0.25 per cent. at the normal speed when  $z = 2$ . It is therefore seldom of sufficient importance to be taken into account in the case of a reaction turbine. Other factors, such as the form of the blades, have more influence on the variation of  $DH$  and  $M$  with speed.

It is evident that the efficiency and the mass-flow would be increased by any modification of the blade-form, especially of the inlet angle, which permitted an increased proportion of the energy rejected in one stage to be carried over to the next. This would be represented in equation (1) by an increase in the value of the constant  $f_1'$ , giving a proportionate increase in  $z^2$ , and in the product  $Mz$  in equation (8).

It is evident that the value of  $f_1'$  is capable of including the effect of moderate variations of the blade-form on the mass-flow, but it is a debatable point whether the expression  $f_1'(z - 1)^2/z^2$ , varying as the ratio of the squares of the tangential components of the relative velocities of entrance and discharge, will suffice to represent the variation of the loss with speed. It seems probable

that, apart from leakage, the most important part of the loss occurs at entrance, or in carry-over from one blade-ring to the next. Martin estimates the loss at 50 per cent. of the kinetic energy  $U'^2/2g$  at entrance. This gives nearly the same result as the formula here proposed when the value of  $z$  is in the neighbourhood of 2, but gives a rather slower rate of variation of the loss with speed. It would appear, however, that the percentage loss in carry-over should not be constant, but should increase with the obliquity of entrance. It is possible, for this reason, that the formula here proposed may prove preferable in practice to the assumption of a constant percentage of loss, because it makes some allowance for the increase of loss with obliquity. But the main point in its favour is that it leads to the simplest possible expression for the variation of efficiency with speed, consistent with the experimental result that the mass-flow is approximately independent of the revolutions. This result cannot be generally true unless the percentage loss in carry-over increases with the obliquity in the manner specified. The simplest way of testing this point is by taking an extreme case in which all losses are supposed to be absent except the loss under discussion.

Taking the same data as in the last example, but with  $f'_1 = 1$ , and  $f'' = 1$ , to eliminate other losses, and with the same value of  $\int aVdP$ , namely, 13.21 at  $z = 1$ , we find  $uz = 198$ ,  $M = 184.2$  in place of 121.1, showing the effect of the increase of  $f$ . But the initial pressure has been taken as 164.7 and the pressure-drop has been increased to 41.5 lbs., for comparison with the next example. Under the same conditions with  $u = 0$ , and  $DH = 0$ , we find  $\int aVdP = 18.68$ , and the tangential component of the steam-speed,  $uz = 196.4$ , giving  $M = 182$  for the same pressure-drop  $DP$ . The diminution of  $M$  with increase of steam-speed may appear at first sight anomalous, but is exactly accounted for by the increase of mean volume from  $V = 3.097$  at  $z = 1$ , to  $V = 3.208$  at  $u = 0$ , owing to the fact that the final value of  $H$  is 18.21 less when  $z = 1$  than when  $u = 0$ .

The approximate constancy of the steam-speed and mass-flow illustrated in the above example, depends on the percentage loss increasing with obliquity in the ratio of the square of  $(z-1)/z$ , which gives the nearest approach to constancy which can be obtained on any simple hypothesis for a given pressure-range, since both  $M$  and  $uz$  cannot be exactly constant owing to the variation of the mean volume. If the percentage loss in carry-over is

independent of the obliquity, the steam-speed ceases to be independent of the blade-speed, and the variation of the mass-flow in some cases may be very considerable. The variation is greatest when there is no loss in carry-over, or if frictionless adiabatic flow is assumed, as in the discussion of the analogous case of discharge through a nozzle.

When the flow is assumed to be frictionless, the pressure-drop for the first ring of guide-blades, starting from rest, is obtained in terms of  $M$  by the usual formula for a nozzle. The flow through each successive blade-ring after the first is given by the equation,

$$aVdP \{1 - (1440/18g) (M/X')^2 V/P\} = (2z - 1)u^2/2Jg = AW',$$

.....(10)

which expresses the fact that the available energy has to supply the equivalent of the work done by the change of relative velocity from  $U'$  at discharge to  $U''$  at entrance, and the additional kinetic energy due to the increase of  $U'$  with  $V$  at each successive blade-ring. The form of the equation shows that the mass-flow will reach a limit when

$$(M/X')^2 = (18g/1440) P/V \text{ (F.P.C.)}, \text{ .....(11)}$$

which is the usual expression for the maximum discharge through a nozzle in terms of  $P$  and  $V$  in the throat, where  $X' = X \cos \alpha$ , in terms of the annular area  $X$ , neglecting the thickness of the blades. This maximum will be reached at the first blade-ring when  $u = 0$ , if the pressure-ratio exceeds the critical value  $P''/P' = 0.5457$ ; in which case the corresponding value of  $M$  for  $X = 853$  sq. in., or  $X' = 291.7$ , will be 704 lbs./sec. with  $P' = 164.7$ . With the pressure-drop  $DP = 41.5$  lbs. (less than the critical value), as in the last example, the value of  $M$ , when  $u = 0$ , will be 635 lbs./sec., diminishing rapidly to 269 lbs. at  $u = 41.8$  ft./sec., and to 176 lbs. at  $u = 88.6$ , and reaching a minimum  $M = 134.2$ , the same as the maximum in the previous example, when  $z = 1$ , at  $u = 193$  ft./sec.

The wide range of variation of  $M$  in this case, from 635 lbs./sec. at  $u = 0$ , to 134 lbs./sec. at  $z = 1$ , resulting from the assumption of absence of loss in carry-over, illustrates the importance of this loss as affecting the variation of  $M$  with speed; but the condition of frictionless flow differs so widely from that actually obtaining in a reaction turbine that the result might be regarded as without practical significance. The range of possible variation of  $M$  with speed is greatly reduced when a constant percentage of loss in carry-over is assumed, but the same type of variation still persists to a



marked extent even when the loss is as high as 50 per cent. In order to represent a loss of 50 per cent., we have merely to add the term  $U'^2/4Jg$  to the right-hand side of equation (10) for frictionless flow. Repeating the calculation for the same pressure-range with this addition, we find that  $M$  varies with speed from 171 lbs./sec. when  $u = 0$ , to 129 lbs./sec. when  $z = 1$ , and  $u = 186$  ft./sec. If  $M$  is to be approximately independent of the speed, we are driven to the conclusion that the percentage loss in carry-over cannot be constant, but must increase with the obliquity of entrance, as appears probable on theoretical grounds. It is quite possible that the effect may vary in slightly different ways in different cases owing to secondary causes which cannot be represented in the fundamental equations of flow, but it appears probable that the simple assumption involved in equation (1), which greatly facilitates calculation, will be sufficiently accurate for all practical purposes, in the majority of cases, as representing the effect of variation of speed on the efficiency. It must be understood that the application of the formula is not confined to the case of variation of blade-speed at constant pressure. The variation of blade-speed is usually accompanied by variation of steam-speed in some of the expansions. All such variations are taken into account in a simple and consistent manner by the proposed method of calculation, which includes all primary causes which may affect the velocity-ratio, whether variations of speed, or pressure, or dimensions, or state of the steam.

**153. Variation of Pressure.** In the case of a complete turbine, variation of initial or final pressure may affect different expansions in very different ways owing to the condition of continuity of mass-flow; but it will be advantageous to consider first the case of a single expansion under arbitrary conditions, in order to prove the applicability of the method in extreme cases, which are very suitable as a means of testing the formula, though they may seldom occur in actual practice.

To take first a simple case, we may suppose the available energy to remain constant while the initial pressure  $P'$  is varied. If the blade-speed  $u$  is also constant, equations (1) and (2) show that  $z_m$ ,  $DH$ , and  $f$ , will be constant, and equation (3) shows that  $M$  will vary directly as the pressure-drop  $DP$ . If we suppose in addition that the initial pressure is regulated by throttling, the initial value of  $H$  will remain constant, and the pressure-ratio  $P'/P''$  will also be nearly constant, in which case the pressure-drop  $DP$  will

be nearly proportional to the initial pressure  $P'$ , so that  $M$  will vary as  $P'$ . If  $H'$  varies (e.g. with superheat) while  $P'$  and  $P''$  are constant,  $z_m$  will increase with  $H'$ , and  $M$  will diminish. If  $H'$  increases, while  $P'/P''$  remains constant,  $z_m$  will increase, and  $M$  will increase less rapidly than  $DP$  or  $P'$ . The variation of  $M$  is readily deduced from the equations for any given case that may arise, but it is necessary to beware of assuming generally that  $M$  will be proportional to  $P'$  if  $P'/P''$  is constant. This result is very nearly true for regulation by throttling at constant speed, and is of interest as explaining the straightness of the power-consumption line illustrated in Fig. 28, § 123, for that particular case.

If we substitute  $z_m = V_m (144M \tan \alpha / uX)$  from (6) in equation (3), we obtain

$$DP/V_m = (DP)^2 / \int V dP = (144N/gf_1') (M \tan \alpha / X)^2, \dots (12)$$

which shows that the proportionality of  $M$  to  $DP$  when  $\int V dP$  is constant rests on taking the mean value of  $V$  by the formula  $V_m' = \int V dP / DP$  at equal intervals of  $P$ . It remains to consider how far this assumption may require modification in extreme cases.

If we make the same substitution for  $z_m^2$  from (6) in equation (1), the equation for  $M^2$  takes the form

$$\int V dP / V_m^2 = (144N/gf_1') (M \tan \alpha / X)^2, \dots (13)$$

which shows that  $M$  varies directly as the mean density and as the square root of the available energy, which is equivalent to assuming that the losses vary as the square of the velocity, the only practicable assumption in a case of this kind. It is evident from the manner of their derivation that equations (12) and (13) should be identical, so that they afford a convenient test of the conditions under which (1) and (3) are consistent in extreme cases.

It has already been shown that, if the blade-angles are adjusted by the condition  $V \tan \alpha = V_m' \tan \alpha_m$ , equations (1) and (3) are exactly consistent for all pressure-ranges or values of  $N$ , in the case of dry steam, because the expansion curve in this case is of the type  $PV = kP^{2/13}$ , and requires the mean volume  $V_m' = \int V dP / DP$ . This case is of special interest for theoretical purposes, because it is easy to imagine the angles adjusted by this condition to secure the maximum efficiency. But in the case of a *given* machine, the adjustment could be exact only for a particular pressure-range, so that the case in which the blade-angle is constant is of greater practical interest in considering the effect of the variation of pressure in extreme cases.

When the blade-angle is constant, the same value of  $V_m'$  affords a sufficient approximation for most practical purposes for the normal range of one expansion, or for any smaller range, as previously illustrated, but it may be desirable to push the approximation further in special cases. Neglecting for the moment the correction for discontinuity depending on the value of  $N$ , the appropriate value of  $V_m$  when  $\alpha$  is constant, is that denoted by  $V_m''$  and given by equation (7), corresponding to equal intervals of  $P/V$ . The value of  $V_m^2$  in equation (18) has to be taken at the same intervals, but represents the mean of the *squares* of the values of  $V$  which is not quite the same as the square of the mean value  $V_m''$ . It happens however that the mean of the *squares* of the values of  $V$  taken at equal intervals of  $P/V$  along the curve  $PV = kP^m$ , is accurately represented by the product  $V_m'V_m''$  between the same limits.

It follows that equations (12) and (18), or (1) and (8), remain consistent also in the case in which  $\alpha$  is constant, provided that the appropriate mean values of  $V$  and  $z$  are employed. The appropriate value of  $V_m$  in equation (12) is  $V_m''$  from equation (7), and the appropriate value of  $V_m^2$  in equation (18) is  $V_m'V_m''$ , and of  $z_m^2$  in equation (1) is  $z_m'z_m''$ . The same value of  $z_m$ , namely  $z_m''$  corresponding to  $V_m''$ , is required in both equations (2) and (8), but in order to find  $z_m''$  from equation (1), it is necessary to insert the factor  $z_m''/z_m' = V_m''/V_m'$ , giving

$$z_m''^2 = f_1' \int aV dP V_m''/V_m' Z = af_1'(2-m)(DP)^2/ZD(P/V). \dots (1a)$$

Eliminating  $z_m''/DP$  between (1a) and (8), we obtain the equation for  $M''$ ,

$$144N(M'' \tan \alpha/X)^2 = gf_1'D(P/V)/(2-m). \dots (14)$$

The value of  $M''$  obtained from this equation is the same as that given by equation (8), or (12), or (18), but requires correction, as shown by (18), for the effect of discontinuity of expansion on the values of  $V_m'$  and  $V_m''$ , by dividing  $M''$ , as given by (8) or (14), by the square root of the product of the correction factors,  $1 + DV/4NV_m'$  and  $1 + DV/4NV_m''$ , which may usually be taken as equal to either factor separately, when the correction is small.

In applying these equations, the value of  $z_m$  is first found from (1), (2), and (8) in the usual way, which will give sufficiently accurate values of  $V''$  and  $m$  for finding  $V_m'$ ,  $V_m''$ , and deducing the small corrections. But, except in extreme cases, the corrections may usually be neglected.

Another instructive method of obtaining equation (14) for  $M''$ , when  $\alpha$  is constant, is to write the equation for a single step in the form

$$aV_m dP = (z/V)^2 K''^2 u^2 / 2Jg = (z/V)^2 V_m^2 (1 + dV/V_m) u^2 / 2Jg,$$

where  $V_m$  is the mean value of  $V$  required in  $aVdP$ , and  $V''$  the final value for the step considered. The ratio  $z/V$  is constant, and proportional to  $M$ , as shown by equation (6). The correction factor  $1 + dV/V_m$  is taken as a sufficient approximation to  $(V''/V_m)^2$ . Transferring  $V_m^2$  to the left side of the equation, and integrating  $dP/V_m$  on the assumption  $PV = kP^m$  for the  $2N$  steps of the expansion, the equation takes a form identical with (14) except that the correction factor for  $M''$  becomes  $1 + \log_e r/4N$ , where  $r$  is the expansion-ratio. This factor is practically the same as that previously given, but is a little less accurate in extreme cases. The correction factor must be omitted from the value of  $M''$  required in equation (8). Conversely, the *observed* value of  $M$  must be *multiplied* by the correction factor before insertion in (8) for finding  $z_m''$  and  $DH$ , when  $DP$  and  $M$  are known.

As a numerical example of the application of these corrections in an extreme case, we will take the expansion previously considered, with  $X = 853$  sq. in.,  $Z = 2.480$  cal. C., but we will suppose the pressure-range extended from  $P' = 164.7$  (dry sat.) to  $P'' = 68$  lbs. abs., making the logarithm of the pressure-ratio four times the normal. We will also suppose the number of stages reduced to a quarter,  $N = 4$  in place of 16, the speed  $u$  being doubled to keep  $Nu^2$  the same. The corrections in this case will be about twenty times as large as for the normal range, and will afford a better test of the accuracy of the method of calculation. Since the value of  $f$  is unimportant for the present purpose, we may put  $f_1' = f'' = 1$ . The numerical formula for  $M$  from (13) becomes

$$M^2 = 5387 f a V dP / V_m^2.$$

From equations (1) and (2), with a preliminary estimate  $z = 4$ , we find as a second approximation,

$$\begin{aligned} z &= 4.174, & DH &= 18.22, & DaPV &= 4.83, \\ f a V dP &= 48.21, & V_m' &= 4.181, & V'' &= 6.612. \end{aligned}$$

Whence, by substitution of this value for  $z$  in (8), with  $\alpha = 70^\circ$ , we obtain  $M = 864.2$ , which is the correct answer for the case in which the blade-angles are adjusted by the condition

$$V \tan \alpha = V_m' \tan 70^\circ.$$

The same result is obtained from (12) or (18) by putting

$$V_m = V'_m = 4.181,$$

as found above. No correction for pressure-range or discontinuity is required with this method of adjusting the blade-angles. The mean of the actual values of  $\tan \alpha$  for the separate blade-rings will not be  $\tan 70^\circ$ , but is readily obtained, if required, from the mean of  $1/V$ , since  $(\tan \alpha)_m = V'_m \tan 70^\circ (1/V)_m$ , where

$$(1/V)_m = 1/V'_m + D(1/V)/4N^*,$$

giving  $(\tan \alpha)_m = \tan 70^\circ (1 - 0.0536)$ . If the actual mean value of  $\tan \alpha$  were given as  $\tan 70^\circ$ , the value of  $M$  would require reduction by the same factor, giving  $M = 864.2 - 19.5 = 844.7$ . When  $z$  is constant, the values thus obtained will be exact in the case of dry steam, because the expansion curve coincides so very closely with the type  $PV = kP^m$ , giving  $V'_m = \int V dP / DP$  for the required value of  $V_m$ . They will also be practically exact for saturated steam in the present case, because the actual expansion curve, with  $DH = 18.2$ , falls only 7 cal. C. below the saturation line, so that there would be little change of volume even if the steam did not remain dry and supersaturated, as would probably be the case in practice.

For the case in which  $\alpha$  is constant, we must substitute  $V'_m V''_m$  for  $V_m^2$  in equation (18), and  $z'_m z''_m$  for  $z_m^2$  in equation (1), because the variation of  $z$  is considerable when the pressure-range is large. Using the value of  $V''$  already found at  $P'' = 68$ , with

$$m = DaPV / \int aV dP = 0.1002,$$

we obtain  $V''_m = 3.896$  from (7), giving  $z''_m = 4.053$  from (1 a). This requires a smaller value of  $DH$  from (2), and gives finally,

$$\begin{aligned} DH &= 17.62, & \int aV dP &= 43.29, & V'_m &= 4.188, \\ V'' &= 6.685, & V''_m &= 3.900, & D(P/V) &= 49.65. \end{aligned}$$

With  $m = 0.0970$  (corrected), we obtain  $M'' = 374.8$  either from (18) or (14), uncorrected for discontinuity of expansion. The correction factor  $1 + DV/4NV_m = 1.0556$ , which gives finally

$$M = 374.8 / 1.0556 = 355.0.$$

The correction factor  $1 + \log_e r / 4N$  comes to 1.0548, and gives  $M = 355.4$ .

It will be seen that the correction for discontinuity becomes

\*  $D(1/V) = 1/V'' - 1/V' = -0.2078$  (negative), excluding the initial value  $1/V'$ , but including the final value  $1/V''$ , in the mean  $(1/V)_m$ .

quite appreciable in extreme cases, when the pressure-range is large and the number of stages small, but the required correction is easy to apply, and the whole calculation is very similar to finding the discharge through a nozzle when the pressure-ratio is less than the critical. It will also be observed that the arrangement with  $z$  constant is appreciably more efficient than with  $\alpha$  constant for large pressure-ranges, giving in the present case a larger heat-drop, 18.22 in place of 17.62. But for the usual range of one expansion, neither the correction for discontinuity nor the difference of efficiency may be expected to exceed a fraction of 1 per cent. Both may safely be omitted unless either is the subject of special investigation.

**154. Step by Step Method.** When  $\alpha$  is constant and  $M$  is given, it is comparatively easy to find the correct result for any pressure range or value of  $N$  by calculating each step in succession, especially when the number of steps is small. This method is useful and instructive as a verification of the corrections required in the case of the continuous integral, but would be unnecessarily tedious for practical application, because the separate steps have to be calculated to the same order of accuracy as the final result in order to avoid cumulative errors.

Taking the previous case as an example, with eight steps, and  $M = 855$ , we have for each step the relations,

$$[aVdP = 0.80064V''^2 \dots (1), \quad DH = 0.810(2z - 1) \dots (2),$$

and

$$z = 0.9845V'' \dots (3).$$

The simplest way of performing the verification is to start with the final state and work backwards, since  $V''$  and  $z''$  and  $DH$  are given for each step in this case. But it is more instructive as an exercise in interpolation to start with the initial state, because  $V''$  has to be estimated for each step in advance.

The procedure is as follows. Estimate  $V''$ , giving  $z$  from (3),  $DH$  from (2),  $DaPV$  or  $DPV$  from (9), whence  $D \log PV$ .  $\log(P'/P'')$  is then found from (1) by writing it in the form

$$D \log P = 0.80064V''^2 D \log PV / DaPV,$$

giving  $\log P$  and  $P''$ .  $V''$  is then calculated from  $P''$  and  $H - B$  as a verification. If the result differs from the first estimate of  $V''$ , the calculation should be repeated with a second estimate, from which the correct result can always be found by interpolation, if

no mistakes have been made. The following table shows the arrangement of the work, but no interpolation was required, except in the last step, where it was necessary owing to the rapid increase of  $V''$ , and the difficulty of estimation. The first line of the table gives the initial state. The first column gives, first the estimated value of  $V''$ , and second that found from  $P''$  and  $H - B$  at the end of the calculation for the step. The differences  $DH$ ,  $DaPV$ , and  $D \log P$ , are found with the slide-rule as already indicated, but the difference under  $\log aPV$  is obtained from the difference of the logs of the initial and final values of  $aPV$ , which difference must be taken to four significant figures to give sufficient accuracy in the calculation of  $D \log P$ . The differences of  $P$  are not required in the calculation, but are given to show the rapid increase.

Table II.

Step-by-step Method, with eight steps,  $\alpha = 70^\circ$ ,  $M = 855$ ,  
 $X = 858$  (F.P.C.).

No.	$V''$	$z$	$H - B$	$aPV$	$\log aPV$	$\log P$	$P$	$P/V$	$[aVdP$
0	2.785		203.54	47.17	673666	21669	164.70	59.14	
1	2.920	2.875	1.472	0.351	003244	02368	8.74	5.72	2.562
	2.919		202.068	46.819	670422	19301	155.96	53.42	
2	3.080	3.032	1.570	0.374	003483	02656	9.24	5.75	2.852
	3.078		200.498	46.445	666939	16645	146.72	47.67	
3	3.270	3.220	1.687	0.402	003775	03019	9.86	5.83	3.215
	3.271		198.811	46.043	663164	13626	136.86	41.84	
4	3.514	3.460	1.836	0.437	004142	03519	10.66	5.92	3.713
	3.514		196.975	45.606	659022	10107	126.20	35.92	
5	3.832	3.773	2.029	0.483	004624	04226	11.70	6.04	4.414
	3.832		194.946	45.123	654398	05881	114.50	29.88	
6	4.282	4.216	2.304	0.548	005307	05337	13.24	6.22	5.511
	4.281		192.642	44.575	649091	00544	101.26	23.66	
7	4.997	4.920	2.741	0.652	006399	07366	15.80	6.55	7.505
	4.997		189.901	43.923	642692	93178	85.463	17.11	
8'	6.600	6.487	3.719	0.887	008860	13078	22.221		
	6.618		186.182	43.036	633832	80100	63.242	7.62	13.257
8''	6.700	6.596	3.870	0.901	009001	13482	22.807		
	6.674		186.031	43.022	633691	79696	62.656		
8°	6.641	6.538	186.12	43.030	633771	79934	63.00	9.49	43.029

It will be seen that the results agree very closely with that found by the integral method. The final pressure being the same, the final volume differs by only 1 in 1000. The differences of  $P/V$  are nearly constant at first, but increase somewhat rapidly towards the end. The value of  $V''$  required for the next step in each case is most

readily estimated from  $aPV/(P/V)$ , since  $PV$  changes slowly. Thus to estimate the value required for the fourth step, the drop of  $P/V$  was estimated as 5.98, giving  $P/V = 85.91$ , and the value of  $PV$  was estimated as 45.61/a, giving  $V^2 = 9.722 \times 45.61/85.91$ , or  $V = 8.514$ , which came out right. The value of  $\int aVdP$  from the table comes out 43.08, which is only 0.25 less than that calculated by the integral method, in spite of the wide range of variation of  $m$  shown by Table II, from 0.1870 for the first step, to 0.0674 for the last step. The percentage error in  $V_m'$  is the same as that in  $\int aVdP$ , but that in  $V_m''$  is somewhat greater owing to the error of the assumption that the intervals of  $P/V$  are equal. As a result, the actual mean value of  $z_m''$  from the table, namely 4.004, is somewhat less than the value 4.053 calculated from  $V_m''$ , and the actual heat-drop  $DH = 17.42$  is also less than the calculated value,  $DH = 17.62$ , but this makes an error of only 1 in 1000 in the final volume, the effect of which on  $D(P/V)$  or  $M$  is inappreciable. Since the integral method is capable of giving a satisfactory result in such an extreme case, it is a reasonable inference that it will be sufficiently reliable for all ordinary purposes, although it may appear at first sight unjustifiable to apply such a method when the differences are so far from being infinitesimal.

Equation (14) for  $M$  does not contain  $u$  explicitly, and the value of  $M$  will be independent of variation of speed except in so far as it affects  $DH$  and  $V''$ . But if  $N$  is varied while  $Nu^2$  is kept constant,  $DH$  and  $V''$  will remain the same for a given pressure-range, and  $M$  will vary inversely as the square root of  $N$ , apart from the small correction depending on  $DV/4N$ . In this case the limiting value of  $M\sqrt{N}$  when  $N$  is large, depends only on the pressure-range, and the value of  $M$  for any value of  $N$  may be deduced from the limiting value of  $M\sqrt{N}$  by dividing it by  $\sqrt{N}$  and by the correction factor  $(1 + DV/4NV_m')$ . The limiting value of  $M\sqrt{N}$  is readily obtained from (14), and will give good results in all practical cases; but when  $N$  is very small in comparison with the pressure-range, e.g.  $N = 1$ ,  $P'/P^2 = 8$ , the correction  $DV/4N$  ceases to be accurate because the difference between the mean volume and the final volume in each step can no longer be taken as equal to  $dV/2$ . If accurate results are required when  $N = 1$ , it is preferable to calculate the two steps separately, and is nearly as easy as working out the values of  $V''$  and  $m$  by the integral method. The integral method holds accurately in the limiting case when  $N$  is large, and affords a convenient standard of reference for other cases.



**155. Maximum Value of the Discharge  $M$ .** When the final pressure is reduced, keeping the initial pressure constant, for an expansion of  $N$  stages, the value of the discharge  $M$  reaches a maximum, as in the case of a nozzle, but at a much lower final pressure, owing to the loss of available energy in work and friction. The curves shown in the annexed figure illustrate the variation of  $M$  with increase of pressure-drop  $DP$  for the cases considered in

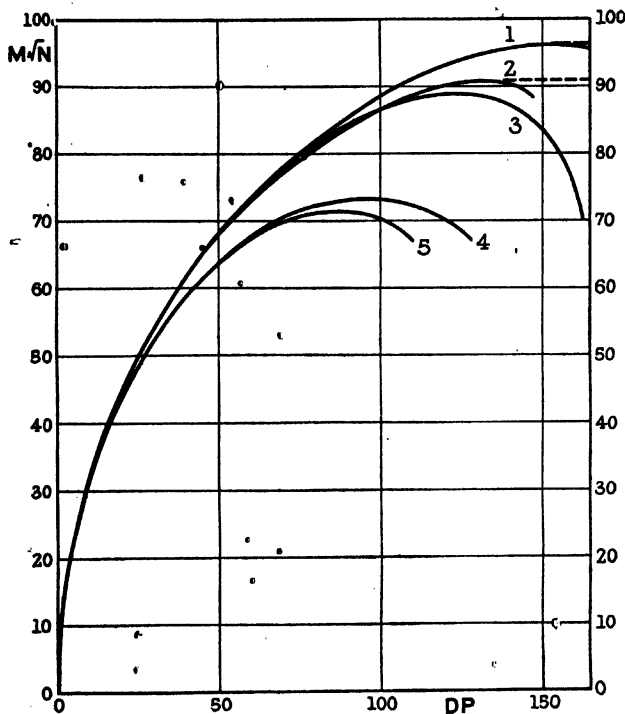


Fig. 33. Variation of Discharge with Pressure-drop.

the previous section, taking the initial pressure as 150 lbs. above atmospheric, or 164.7 abs. Up to a pressure-drop of 60 or 70 lbs., or a pressure-ratio  $P'/P'' = 8/2$ , exceeding the limit usual in practice for a single expansion, the differences between different cases when the dimensions are given, rarely amount to so much as 1 per cent., and are seldom worth considering for ordinary purposes.

Beyond this point the curves begin to diverge, and are of special interest from the theoretical standpoint.

The curves in the figure are drawn for the dimensions  $X = 100$  sq. in.,  $\alpha = 70^\circ$ , and  $Z = 10$  cal. C. Since  $M$  is proportional to  $X/\tan \alpha$ , corresponding values for other dimensions are readily deduced. The quantity actually plotted in curves (1) and (3) is not  $M$ , but the limiting value of  $M\sqrt{N}$  when  $N$  is large. The actual value of  $M$  for any particular value of  $N$  is obtained by dividing the ordinate of the curve by  $\sqrt{N}$ , and by the correction factor  $1 + DV/4NV_m'$  when required. The upper curve, marked 1, in the figure represents the limiting value of  $M\sqrt{N}$  when  $\alpha$  is constant as given by equation (14). There is a maximum at a low pressure, about 8 lbs. abs., but the values at such low pressures are somewhat uncertain owing to the variation of  $m$ . The order of uncertainty is roughly indicated by the thickness of the line.

The intermediate curve (2) in the figure represents the effect of dividing the ordinates of the upper curve by the correction factor  $1 + DV/40V_m'$  corresponding to  $N = 10$ , which has the effect of raising the position of the maximum to a pressure of nearly 80 lbs. abs. The correction for any other value of  $N$  is readily obtained by a proportional reduction. The position of the maximum is further raised for lower values of  $N$ . The pressure at which the maximum occurs when  $\alpha$  is constant is determined by equation (11) for the velocity of sound at the exit, and it is of interest to observe that this condition agrees in each case with the position of the maximum indicated by the application of the correction factor. Thus when  $N = 10$ ,  $M\sqrt{N} = 90.6$  corrected,  $M = 28.65$ , and condition (11) is satisfied at  $P'' = 29.4$  lbs.

After reaching the maximum, the discharge would remain constant for any lower final pressure, as indicated by the broken line in the figure. The interpretation of the falling part of the curve beyond the maximum is the same as in the analogous case of a nozzle. The ordinate of the curve represents in reality  $M\sqrt{N} \tan \alpha/X$ , and can be employed for calculating appropriate values of  $M$ ,  $X$ ,  $N$ , or  $\tan \alpha$ , to suit given conditions for any pressure-drop, with the same initial state and value of  $Z$ .

The value of  $Z = Nu^2/Jg$ , makes comparatively little difference to the result for  $M$ . The value  $Z = 10$  cal. C., may be taken as representing the case of a turbine of high speed and efficiency, just as the value  $Z = 2.48$  cal. C., taken in the previous example, represents the case of a slow-speed marine turbine in which the

efficiency or the turbine itself is sacrificed to accommodate that of the screw-propeller. As an illustration of the effect of  $Z$  on  $M$ , we may employ the curve for  $Z = 10$  to find  $M$  for the data of the previous example with  $P'' = 68$ ,  $X = 858$  in place of 100, and  $N = 4$ . The ordinate of the limit curve at  $DP = 101.7$  is 88.9, which must be multiplied by  $8.58/2$ , giving 379 as the uncorrected value of  $M$ . The correction for  $N = 10$  is 2.2 per cent., giving 5.5 per cent. for  $N = 4$ . The corrected value of  $M$  is 359 with  $Z = 10$ , whereas the value previously found with  $Z = 2.48$  was  $M = 355$ . The difference is due to the lower mean density resulting from the smaller heat-drop at the lower value of  $Z$ .

The curve marked 3 in the figure represents the variation of  $M/\sqrt{N}$  with  $DP$  for the case in which the blade-angles are adjusted by the condition  $V_c \tan \alpha = V_m' \tan 70^\circ$ . The divergence of this curve from the limit curve 1 for  $\alpha$  constant is negligible at  $DP = 65$ , and amounts to less than 1 per cent. at  $DP = 90$ . The difference between curves 1 and 3 corresponds with the difference between  $V_m''$  and  $V_m'$ , which increases rapidly at low pressures. The value of  $M$  for any given  $N$  is obtained by dividing the ordinate of curve 3 by  $\sqrt{N}$ , but the correction factor  $1 + DV/4NV_m'$  is not required if the angles are adjusted by the given condition. The maximum in this case occurs at the same point,  $P' = 39.1$  or  $DP = 125.6$ , for all values of  $N$ , and is determined from equation (12) or (18) by finding the position of the maximum value of  $DP/V_m'$ , or  $DP^2/\int V dP$ , which gives the simple condition  $V'' = 2V_m'$  for the relation between the final volume and the mean volume when  $M$  is a maximum. Condition (11) for the velocity of sound does not apply in this case, because by hypothesis the discharge angle  $\alpha$  is reduced, increasing the aperture at exit, whenever the final pressure is reduced. The cross-section of the throat is not constant, but is a function of the final pressure. Except in the case  $N = 1$ , the velocity of sound cannot be reached until after the maximum determined by (12) or (18) is passed.

For very small values of  $N$  the result may be appreciably affected by different assumptions with regard to the distribution of the losses between blade-friction, carry-over, etc. The value  $f_1' = 1$ , taken in the present calculation, is equivalent to supposing that the energy required to make up for blade-friction, and for the acceleration of the axial component  $U$ , is supplied by energy carried over from the previous stage, since by equation (1) the whole of the available energy  $aVdP$  is expended in the tangential

component  $zu$  when  $f_1' = 1$ . In practice any such losses are included in the value of  $f_1'$  determined experimentally, and it is inexpedient to attempt any further analysis. Since the steam must always be moving with at least the appropriate axial velocity at the beginning of each expansion, the assumption represented by equation (1) is justifiable provided that the pressure  $P'$  is measured at the beginning of each expansion, as would usually be the case, especially if the number of stages is reasonably suited to the pressure-range. The cases in which  $N$  is small and  $DP$  large are of little practical importance, but it may be worth while to take the maximum discharge with  $N = 1$  as an illustration of the limit of error of the correction factor  $1 + DV/4NV_m$  in the most extreme case possible in practice.

The curve marked 4 in the figure represents the application of the correction factor  $1 + DV/4V_m$  for the case  $N = 1$  to the limit curve 1, and shows a maximum  $M = 73$  at  $DP = 95$ . The step-by-step method (with two steps) for the same case gives the curve marked 5 with a maximum  $M = 71.4$  at  $DP = 87$ , with  $V'' = 5.14$ , satisfying condition (11) for the velocity of sound, which is not exactly satisfied by curve 4. Otherwise the agreement of the two curves is surprisingly close.

Although such extreme cases as are here considered cannot occur in the ordinary running of a turbine, they afford useful illustrations of methods of calculation, and show that the simple equations (1), (2), and (3) are fairly trustworthy for ordinary purposes. The equations for the separate expansions can be utilised in actual tests by observing the pressures at intermediate points, which no doubt is frequently done though the results are too illuminating to publish. It would be comparatively easy to test the effects of variation of clearance, of modifications in the form of the blades, and of many other details of construction, which cannot be investigated satisfactorily without a reasonably simple theory including all the primary factors on which the effects depend.

From the point of view of the present work, the most interesting effects would be those depending on the change of state of the steam, which still remain obscure, but could be greatly elucidated by a well designed series of experiments. There is already a strong presumption that the steam will not follow the state of saturation as generally assumed, but will remain practically dry and super-saturated until a certain limit is reached. The actual position of this limit is still uncertain, but it would in all probability be clearly

indicated by the pressure observations in conjunction with the known dimensions. Beyond this limit the theory is less certain, but the effects of initial superheat appear to show that a marked degree of supersaturation persists in rapid expansion. This would probably produce secondary effects on the flow, as explained in Chapter XVI, which do not appear to have been anticipated, and require further experimental tests for their proper elucidation.

The case which most commonly occurs at low loads in the later stages and expansions, is a great reduction of the pressure-drop and of the velocity-ratio. A comparison of the observed and calculated values of the pressure-drop in such cases would afford a severe test of the applicability of the present theory, but there do not appear to be any published data directly bearing on this point.

## CHAPTER XV

### APPLICATION OF THE ANALYSIS TO A COMPLETE TURBINE

**156. Application to a High-Pressure Turbine.** Equations (1), (2), and (3) can be applied without modification to a complete turbine, provided that  $z_m$  is nearly the same for each expansion, as is usually the case under *normal* conditions of running. For this purpose it is necessary to know the speed and dimensions so that the values of the energy-constant  $Z = Nu^2/Jg$ , and of the expansion constant  $Z' = Nu \tan \alpha/X$ , can be found for each expansion. By adding the equations for all the expansions, as indicated by the symbol of summation  $\Sigma$ , we obtain for the whole turbine,

$$\text{Available energy,} \quad \int aVdP = (z_0^2/f_1') \Sigma Z, \dots\dots\dots(1)$$

$$\text{Heat-drop,} \quad \Sigma DH = H_0 - H_F = (2z_0 - 1) \Sigma Zf'', \dots\dots\dots(2)$$

$$\text{Pressure-drop,} \quad \Sigma DP = P_0 - P_F = (Mz_0/gf_1') \Sigma Z', \dots\dots\dots(3)$$

where  $z_0$  is the mean value of  $z_m$ .

These equations may be employed in various ways, according to the data available and the object of the investigation, either (1) for finding the efficiency and leakage constants from experimental tests in which the heat-drop, pressure-drop, and mass-flow, are observed, or (2) for estimating the probable variations of power, consumption, and efficiency, under different conditions of running, when the efficiency constants are known, or (3) for choosing suitable dimensions in designing a machine for any particular purpose.

In experimental tests, it is always desirable to observe the pressures at points intermediate between the several expansions as a check on the state of the steam, and it may be necessary to calculate each expansion separately if the variation of  $z_m$  becomes excessive. When sufficient data are available, it is possible to find the systematic variation of  $f$  from one expansion to another, but when this is not the case, some allowance can be made for the probable variation of  $f$  by assuming a formula of the type  $1 - l''/x$  for  $f''$  as previously suggested, and finding the average value of  $l''$

from equation (2) when the whole heat-drop is known. It is also possible to represent the effect of leakage on the mass-flow by inserting a similar factor  $1 - l'/x$  in equation (8) from which  $l'$  may be found if  $f_1'$  is known and  $M$  is observed. It seems probable on theoretical grounds that  $l'$  should be less than  $l''$  in the ratio of 2 to 3 nearly. Both can be found if this ratio is assumed.

It is of interest to compare these equations with rules commonly employed in design, such as those given in *Engineering*, Dec. 18, 1907. Such rules depend in the main on assuming a normal type of blade, and a suitable value of the ratio of steam-speed to blade-speed for the purpose required.

*Number of stages.* A rule commonly given for finding the equivalent number of stages  $N_e$  for a complete marine turbine in terms of the diameter  $D$  of the H.P. rotor, is

$$N_e = 5.5 \times 10^3 / D^2 R^2, \dots\dots\dots(4)$$

where  $D$  is the diameter in feet, and  $R$  the revs./min. The equivalent number of stages, allowing for variation of  $u$  in different sections of the turbine, is defined by the condition,

$$N_e u_1^2 = \Sigma N u^2, \text{ where } u_1 = \pi D R / 60 \text{ ft./sec.} \dots\dots\dots(5)$$

Thus, if the diameter of the L.P. rotor is  $\sqrt{2}$  times that of the H.P. the actual number of stages on the L.P. rotor will be about half that on the H.P. if the power is to be equally divided between the two.

Equation (1) of the previous page may be written in the form

$$N_e = (\Sigma N u^2) / u_1^2 = J g f_1' \int a V dP / (\pi z_0 D R / 60)^2, \dots\dots\dots(6)$$

which, with  $f_1' = 0.888$ , reduces exactly to the rule above given, if the available energy appropriate to the usual pressure-range is taken as 340 B.T.U. with  $J = 778$ , provided that  $z_0 = 2.25$  is assumed as a suitable mean value of the speed-ratio, corresponding nearly with an initial value 2 for each expansion. It is justifiable to treat the available energy and  $z_0$  as constants in a particular case of this kind, but the general equation (1) has the advantage of showing how the numerical value of the constant must be modified to suit any other pressure-range, or velocity-ratio, or condition of the steam.

*Steam-Speed.* With  $N_e$  defined as  $(\Sigma N u^2) / u_1^2$ , and  $z_m$  the same (but not necessarily 2.25) in all the expansions, the fraction  $N_1 / N_e$  of the whole energy is available in the first expansion containing

$N_1$  stages. Equation (1), applied to the first expansion, gives for the mean exit velocity  $U_1'$  of the steam from the blades,

$$U_1' = z_m u_1 / \sin \alpha = (J g f_1' [a V d P / N_1 \sin^2 \alpha]^{1/2} = 2918 / N_1^{1/2}, \dots (7)$$

which is independent of  $u$  or  $z$  separately. The numerical value 2918 for the constant assumes the whole available energy to be 840 B.T.U., but the constant evidently varies as the square root of  $[a V d P]$ . This numerical formula is commonly quoted with the value of the constant 2700 or 3000 according as the expansion ratio is less than or greater than 64 (Sothorn, *Marine Steam Turbine*, p. 60), but it seems better to take the constant proportional to  $([a V d P]^{1/2})$ .

The chief difficulty in finding examples for the application of these equations lies in the scarcity of suitable published data. The majority of tests give only the speed and consumption, in relation to the initial state and final pressure, without any details of dimensions. On the other hand, many details of dimensions exist, but these are usually more or less incomplete, and corresponding tests of performance are lacking. In the case of marine turbines, there are great difficulties in the way of obtaining reliable observations of consumption and power, and there is often little or no indication of the manner in which the results were estimated, or of the order of accuracy to be expected. For this reason many of the following examples must be taken rather as illustrations of methods of calculation, which could be applied if complete details were available, than as definite results of experimental tests.

As an illustration of some of these difficulties, we will take one of the trials of H.M.S. *Dreadnought*, which was the subject of many tests as being the first large battleship to be fitted with turbines. There were two complete turbines, port and starboard, each divided into two parts, H.P. and L.P., driving four shafts in all. The total steam was estimated from the feed-pump, but part was employed for driving auxiliaries, the exhaust from which in some trials was taken through part of the L.P. turbines.

In one of the full-speed trials, the steam to the main turbines, excluding auxiliaries, is given as 856,000 lbs. per hour, equivalent to  $M = 49.45$  lbs./sec. for each H.P. turbine, rotor 68" diam., giving  $X = 189$  sq. in. for the first expansion, with  $x = 7/8$ ". Neglecting leakage, and taking  $V' = 2.78$  at the exit of the first blade-row with effective aperture  $0.8X$ , as given by Sothorn (*Marine Steam Turbine*, p. 60) for normal blades, we should find



$U' = 860$  ft./sec. for the initial steam-speed, with  $u = 96.8$  blade-speed at 822 revs./min., giving 8.72 for the ratio  $U'/u$ , and 8.5 for the initial value of  $z$ , or 4.0 for the mean value in the first expansion. High values of the speed-ratio are often ascribed to battleships on the ground of similar calculations, but would generally lead to impossible values of the available energy and incredibly low efficiencies. For this reason it is usually better to deduce  $z$  and  $M$  from the available energy, by equations (1), (2), and (8), which give quite a different result in the present case.

H.M.S. *Dreadnought*, 1906. Full-speed Trials. Starboard turbine.

Boiler pressure, 241 lbs. (gauge), condenser vacuum, 27 inches.

H.P. receiver pressure, 157.5 lbs. (gauge), L.P. receiver, 7.7 lbs. (gauge).

H.P. turbine, 4795 shaft horse-power at 822 revs./min.

L.P. turbine, 7480 shaft horse-power at 387 revs./min.

H.P. rotor, 68" diam., with 6 expansions, each of 12 stages.

L.P. rotor, 92" diam., with 6 expansions, each of 6 stages.

The rule above given for the equivalent number of stages leads to  $N_e = 144$  at 845 revs./min. and  $D = 68''$ , giving 72 stages for the H.P. rotor and 86 for the L.P., since the mean diameter of the blading is very nearly in the ratio 1 to  $\sqrt{2}$  for the two rotors. The blade-heights are selected to the nearest  $1/8''$  to form a geometrical progression with a common ratio  $\sqrt{2}$ , the annular area  $X$  of the first expansion of the L.P. being nearly the same as that of the last expansion of the H.P., because the steam velocity is increased in the ratio of the increase of diameter. The blade-height is the same, 11'', in the last three expansions of the L.P., but the value of  $\tan \alpha$  is taken as 2.747 for normal blades in the fourth expansion, 1.948 for semi-wing blades in the fifth, and 1.874 for wing blades in the last, being reduced in the  $1/\sqrt{2}$  ratio for each expansion in place of increasing the blade-height. The blade-heights are given in the following table, in inches,

Expansion number	1	2	3	4	5	6
H.P. turbine	$7\frac{1}{8}$	$11\frac{1}{8}$	$15\frac{1}{8}$	$21\frac{1}{8}$	$30\frac{1}{8}$	5
L.P. turbine	$3\frac{1}{8}$	$5\frac{1}{8}$	$7\frac{1}{8}$	11	11	11

From which the values of the constants  $Z$  and  $Z'$  for each expansion are calculated at the above given speeds. The sums required in the equations are,

	$\Sigma Z$	$\Sigma Z/x$	$\Sigma Z'$	$\Sigma 1/x$
H.P. turbine	15.68	8.70	50.18	3.40
L.P. turbine	17.42	2.38	5.94	0.79

The sums of  $Z/x$  and  $1/x$  are employed for estimating the effect of tip-leakage on the heat-drop and mass-flow as explained below. Neglecting leakage and receiver-drop in the first instance, and assuming the state of saturation throughout the expansion, with the initial state dry saturated, we obtain the following approximate results for the H.P. turbine.

Estimating  $DH$  as 54 cal. C. we find  $\int aVdP = 88.65$  for the given range.

$$\text{From (1), } z_0^2 = 0.888 \times 88.65/15.68 = 4.992, \quad z_0 = 2.234, \\ 2z_0 - 1 = 3.468.$$

From (2),  $DH = 3.468 \times 15.68 = 54.38$  (neglecting leakage by omitting  $f''$ ).

$$\text{From (3), } M = gf_1' \times 149.8/2.284 \times 50.18 = 88.18. \\ \text{Whence } HP = 2.545MDH = 5247.$$

Similarly for the L.P., with  $DH = 59$ , we find  $\int aVdP = 95.44$ .

$$\text{From (1), } z_0^2 = 0.888 \times 95.44/17.42 = 4.837, \quad z_0 = 2.199, \\ 2z_0 - 1 = 3.398.$$

From (2),  $DH = 3.398 \times 17.42 = 59.20$  (neglecting  $f''$  as above).

$$\text{From (3), } M = gf_1' \times 20.9/2.199 \times 5.94 = 45.45.$$

$$\text{Whence } HP = 6846.$$

Owing to leakage through the H.P. dummy, we should expect the flow through the H.P. turbine to be less than 49.45, namely, half the total feed to the main turbines, but the difference is exaggerated by the neglect of tip-leakage. In spite of the low value,  $M = 88.18$ , the power for the H.P. turbine comes out too high, 5247 in place of 4795, because the heat-drop is too large, owing to the neglect of receiver-drop, and tip-leakage. In the case of the L.P., the apparent flow,  $M = 45.45$ , is much larger than for the H.P. owing partly to the auxiliary exhaust, which was estimated at a total of 27,400 lbs./hour, or 8.95 lbs./sec. for each turbine, and partly to the excess of H.P. over L.P. dummy-leakage. On account of the uncertainty of the feed measurements and the absence of information with regard to the equality of distribution between the port and starboard turbines, no great stress can be laid on the observed values of  $M$ . But the calculated values for different conditions will be relatively correct, and may prove instructive as illustrations of the effects of tip-leakage and supersaturation.

It would evidently be desirable for accurate tests to measure the actual pressures at the first and last rows of blades, because the correction for receiver-drop necessarily depends on the arrange-

ment of the steam-pipes and valves, and cannot be included in the equations. The drop between the last row of blades on the H.P. and the first row on the L.P. is commonly estimated at 5 per cent. of the absolute pressure in the L.P. receiver, but is often larger. For the present purpose we will take the drop as 3 per cent. to or from each receiver, and 7 per cent. to the condenser, giving 167 lbs. for the initial pressure and 23.1 for the final pressure on the H.P. turbine, with 21.7 and 1.6 for the initial and final pressures on the L.P., but the low pressures are generally uncertain.

If the calculation is repeated with the pressures as above corrected for receiver-drop, but otherwise on the same assumptions, neglecting the effects of leakage and supersaturation, we obtain for the two turbines,

H.P.  $z_0 = 2.198$ ,  $DH = 53.12$ ,  $M = 37.18$ ,  $HP = 5023$ .

L.P.  $z_0 = 2.160$ ,  $DH = 57.83$ ,  $M = 44.53$ ,  $HP = 6552$ .

All the values are necessarily reduced by receiver-drop, the loss of power amounting to nearly 5 per cent., but in spite of the low value of  $M$ , the power for the H.P. turbine is still higher than the observed value. The difference between the values of  $M$  for the two turbines remains nearly the same, and is very large as compared with the difference between the values of  $z_0$ , which differ by less than 2 per cent. in the opposite direction.

Seeing that the difference between the mean values of  $z_m$  for the two turbines is so small, it might naturally be expected that the value of  $z_m$  would be nearly the same for all the expansions throughout each turbine. If  $z_m$  were the same throughout, since  $u/X = R/720\alpha$ , we observe that the pressure-drop in each expansion would be proportional to  $1/\alpha$  by equation (8), so that the pressures would form a geometrical progression in the inverse ratio of the blade-heights. But then the energy available in each expansion would vary nearly as  $PV$ , showing that the values of  $z_m$  could not be the same for each expansion in the absence of leakage. Taking  $M = 37.18$ , as found above for the H.P. turbine, it is easy to calculate the corresponding values of  $z_m$  and  $DP$  for the first and last expansions. The values are,

First expansion,  $z_m = 2.65$ ,  $DP = 58.8$   
 Last expansion,  $z_m = 1.85$ ,  $DP = 7.15$  } Leakage neglected,

showing a considerable range of variation of  $z_m$ . The values of  $DP$ , taken as proportional to  $1/\alpha$  would be 48.4 and 8.46 respectively. Neglecting leakage and assuming  $\alpha = 70^\circ$  (constant), the

design requires an expansion ratio of 9, whereas the actual ratio of  $V''$  to  $V'$  is only 6. A lower final pressure would give a more nearly uniform value of  $z_m$ , but the effect of tip-leakage, which is greatest in the first expansion and least in the last, reduces the actual range of variation of  $z_m$  to such an extent that it cannot be neglected in this connection.

**157. Effect of Tip-Leakage.** In order to estimate this effect, we may suppose that the acceleration of the leaking steam is mainly in an axial direction, or that the tangential component of its velocity is unaltered, while the axial component is increased from  $U$  to  $U \sec \alpha$  by the available energy  $f_1' a V dP$  at each blade-ring. If  $l$  is the leakage clearance, the mass-flow of the leaking steam is represented by  $(l/x) \sec \alpha (UX/144V)$ , which will be near enough to represent the mean of the leakages, under the fixed blades and over the moving blades, if  $l$  is the mean clearance, and if  $X$  is calculated from the mean diameter,  $12D + x$ , of the blade-ring in inches, where  $D$  is the diameter of the rotor in feet as in (4).

If there were no leakage, we should have the usual relation  $M = UX/144V$ . The increase of  $M$  due to leakage for a given pressure-drop, is represented by the fraction  $(l/x)(\sec \alpha - 1)$ , which may be taken to be the same for each blade-ring in any one expansion. Similarly the reduction of  $DP$  for a given value of  $M$ , may be represented by introducing the divisor  $1 + 2l/x$  (taking  $\sec \alpha = 3$  for normal blades) in the value of  $Z'$  on the right hand side of equation (3), which has the effect of simply substituting  $x + 2l$  for  $x$  in the expression for  $Z'$ , or  $Z''$ .

The effect of leakage can be investigated separately for each expansion when sufficient data are available, but, if only the whole pressure-drop for the rotor is given, we can still obtain a mean value of  $l$ , corresponding to the ideal case in which the clearance is uniform when the machine is hot.

Since the effective length of the blades is reduced by  $l$ , while the mass-flow is increased as though  $x$  were increased by  $2l$ , the ratio of the working steam to the whole steam will evidently be given by the fraction  $(1 - l/x)/(1 + 2l/x)$  for normal blades. This correction factor may be supposed included in the value of  $f''$  on the right hand side of equation (2), according to the definition of the reaction efficiency, XI, §126. If  $l$  is small and nearly uniform, we may substitute  $(1 - 8l/x)$  for the correction factor in each expansion, so that the factor for the whole turbine becomes,

$1 - 3l\Sigma(Z/x)/\Sigma Z$ , which gives a simple equation for finding  $l$  if  $DH$  is known. Conversely it is easy to estimate the effect on  $DH$  of assuming different values of the clearance.

In applying the correction for leakage to a complete turbine, it is in all cases preferable to observe the pressures at the intermediate points between the expansions, and to work the results for each expansion separately; but, if only the initial and final pressures are available, as in the present example, a preliminary approximation may be obtained in the following way. Equation (2) presents no difficulties, because the values of  $DH$  and  $Z$  are nearly the same for each expansion, and the equations can be added, even if  $x_m$  is not quite constant, without introducing material errors in the mean. But, in equation (8), the values of  $DP$  and  $Z'$  vary widely from one expansion to another, and the summation cannot be performed satisfactorily by substituting the factor  $1 - 2l/x$  for the divisor  $1 + 2l/x$ , which is the usual method of approximation in such cases. Transferring the correction factor  $1 + 2l/x$  to the left hand side, and substituting  $R/720x$  for  $u/X$ , equation (8) for each separate expansion takes the form

$$(x + 2l) DP = Mx_m R \tan \alpha N / 720 g f_1' \dots\dots\dots(8)$$

In adding the separate equations, it will often be permissible to make the approximation  $\Sigma x DP = x_m \Sigma DP$ , where  $1/x_m$  is the mean of the values of  $1/x$ , if  $N$  is the same for each expansion, as in the present example. If the values of  $N$  are different in different expansions, we have for  $x_m$  the equation

$$\Sigma N/x_m = N_1/x_1 + N_2/x_2 + N_3/x_3 + \text{etc.} \dots\dots\dots(9)$$

The sum of the equations for the separate expansions will be

$$(x_m + 2l) \Sigma DP = Mx_m R \tan \alpha \Sigma N / 720 g f_1' \dots\dots\dots(10)$$

in which  $\Sigma DP$  is the whole pressure-drop for the turbine, and  $\Sigma N$  is the whole number of stages. The equation in this form is convenient to use, and will give fairly good results for the effect of leakage on the mass-flow, provided that  $l/x$  is small, and that  $x_m$  does not vary greatly. The value of  $M$  thus found can be verified by calculating the pressure-drop and  $x_m$  for each expansion. The same equation can be employed, if  $M$  is known, to find the mean effective value of  $l$  for the turbine, if a constant value of  $\tan \alpha$  is assumed. But in all such comparisons it is necessary to bear in mind that there may be accidental or intentional variations of  $\tan \alpha$ , which will alter the effective values of  $x$ , as in the case of the wing-blades in the L.P. turbine.

From the above investigation we arrive at the comparatively simple result that the mass-flow through the whole turbine for a given pressure-drop will be increased by the effect of tip-leakage in the ratio  $(x_m + 2l)/x_m$  where  $x_m$  is the mean effective blade-height as above defined, and  $l$  the leakage clearance. But this assumes that  $x_m$  remains the same and is nearly uniform throughout the turbine. In point of fact there will be a small increase in the mean value of  $x_m$  for the whole turbine in consequence of the reduction of  $DH$ , which is easily found from equations (1) and (2); and there will also be a change in the pressure-distribution and in the variation of  $x_m$ , because the pressure-drop will be reduced in the earlier expansions and increased in the later if the whole pressure-drop remains the same.

For the H.P. turbine in the present example, we have  $\Sigma 1/x = 3.400$ , with 6 expansions each of 12 stages, giving  $x_m = 6/3.400 = 1.765$ . Taking  $l = 70$  mils  $= 0.070''$ , as a probable mean clearance over the blade-tips for a turbine of this size,  $M$  is increased by tip-leakage in the ratio 1.905 to 1.765, or from 37.18 to 40.13, which is about 8 per cent. The simultaneous reduction of the heat-drop from 53.12 to 47.20 increases the mean value of  $x_m$  only from 2.194 to 2.204, giving  $M = 39.95$ , in the case of saturated steam. It will be seen that the change of both  $M$  and  $DH$  is considerable, but that the two are nearly independent of each other. The reduction of efficiency, depending only on  $DH$ , amounts to 11 per cent. The horse-power is reduced from 5023 to 4800, agreeing closely with the observed value 4796.

The effect of tip-leakage on the pressure distribution in the present instance is to make the pressure-drop per expansion much more nearly proportional to  $1/x$  than could possibly be the case in the absence of leakage, as previously pointed out. The effect on the first expansion is considerable, reducing the pressure-drop from 58.8 in the absence of leakage with  $M = 37.18$ , to 48.6, with  $l = 0.070''$  and  $M = 40$ , in spite of the increase in  $M$ . The value of  $x_m$  for the first expansion is simultaneously reduced from 2.65 to 2.38. It is easy to calculate the expansions separately when the value of  $M$  is known.

It must be admitted that the effects of tip-leakage in the earlier expansions when the blades are short may introduce some uncertainty in the results, but this only makes it the more necessary to have a simple and consistent theory for comparison with observation. The method above given appears to be the simplest that can

be devised. Most authorities are agreed in taking the ratio of the working steam to the whole steam as  $1 - l/x$  to  $1 + 2l/x$ , when the annular area factor is 3, for each blade-ring, whether fixed or moving. But since the leaking steam cannot contribute anything in either case to the impulse or to the reaction, it might appear at first sight as though the loss of efficiency should be doubled. Morrow (*loc. cit.*, p. 76) takes this view on slightly different grounds, and gives the *effective* proportion of the working steam as being  $(1 - 3l/x)/(1 + 3l/x)$ , which makes the loss of efficiency twice as great as the expression  $(1 - l/x)/(1 + 2l/x)$ , in the limit when  $l/x$  is small, and which leads to improbable results when  $l/x$  is large. To take an extreme case, when  $l = x/2$ , the latter expression would reduce the efficiency to a quarter of the maximum, which is not unreasonable, but Morrow's fraction would make the efficiency *negative*, whereas it is evident that there would still be some balance of useful work. Apart from secondary effects, which are difficult to estimate, it may be admitted that the steam leaking under the fixed blades could not add much to the reaction on the previous ring of moving blades or to the impulse on the succeeding ring, but the energy acquired by the leaking steam, being mainly in an axial direction, is carried over, and tends to increase the reaction on *leaving* the next moving ring. Similarly the steam leaking over the moving blades may contribute little or nothing to the impulse or reaction on the moving blade-ring itself, but the energy acquired in leaking is added to the energy of discharge from the next ring of fixed blades. The fraction  $(1 - l/x)/(1 + 2l/x)$  appears to be of the right order of magnitude to represent the relative drop in efficiency, giving  $(1 - l/x)$  for the relative drop in power, and, although the absolute magnitude of  $l$  may be uncertain, the theory can hardly fail to give useful *comparative* measures of the effects of leakage when combined with experimental tests.

### 158. Calculation for each Expansion in Succession.

The results for each expansion are of special interest when the intermediate pressures are observed, because they tend to throw light on the state of the steam and on possible variations of blade-angle, or clearance, or mass-flow due to by-pass or leak-off from the dummy. In the absence of observations of intermediate pressures, the best that can be done is to assume uniform values of  $l$ ,  $\tan \alpha$ , and  $M$ , in the calculation of the pressure-distribution. The calculation will be made in the present case for the H.P.

turbine on the assumption that the state of the steam is dry and supersaturated throughout, which is possible, because the steam does not quite reach the Wilson limit. But owing to the great extent of the blade-surface in the later expansions, and the uncertainty of the limit at high pressures, it is very likely that condensation would set in before the last expansion was reached. This would be indicated, if the intermediate pressures were available, by a marked change in the pressure-drop as compared with that calculated for dry steam. It is probable that the steam would remain dry in the present case for the greater part of the expansion, but even if the values for the later expansions may not correspond with the actual facts, the calculation will be instructive as an illustration of the method of working out successive expansions.

The calculation for each expansion in the present example starts with a preliminary estimate of  $z_m$  and  $DP$  from equation (8), with  $M = 40$  and  $l = 0.070''$ , giving the numerical relation

$$(x + 0.140) DP = 20.75z_m \dots\dots\dots(11)$$

Thus taking  $z_m' = 2.40$  as a trial value for the first expansion, we have  $DP = 49.06$  from (11) with  $x = 7/8''$ , and  $DH = 7.20$  from (2) with  $f'' = 1 - 0.210/x$ , whence  $z_m'' = 2.391$  from (1), which suggests  $z_m = 2.38$  for the solution. When  $M$  is given, the correct solution for  $z_m$ , as previously remarked, Chapter XIV, § 150, differs from the result of the first calculation of  $z_m''$  from (1) by nearly the same amount as  $z_m''$  itself differs from the first trial value  $z_m'$  assumed in (11), provided that the pressure-drop is small; but it is useful to have a more accurate rule for estimating the correct solution from the result of the first trial when the difference is large.

*Rule.* To find the correct solution from the first trial, multiply the difference  $z_m'' - z_m'$  by  $0.217DP/P''$ , divide by

$$\log(P'/P'') - 0.217DP/P'',$$

and add the result to  $z_m''$ , with due regard to sign.

This rule is easy to apply because the required factors  $DP$ ,  $P''$ , and  $\log(P'/P'')$ , are obtained in the first trial to a sufficient degree of approximation; but it is necessary that the trial calculation should be made to the limit of accuracy required in the final result, and that the trial estimate of  $z_m$  should be within 2 or 3 per cent., to get the final result to 1 in 2000 without repeating the calculation. The numerical factor 0.217 is half the modulus of common logarithms, 0.434,  $\log(P'/P'')$  being taken from a table of common logarithms to the base 10. The rule is based on the assumption



that  $\int aVdP$ , being equal to  $aP_m V_m \log_e P'/P''$ , varies nearly as  $\log (P'/P'')$ , since  $PV$  changes slowly. The rule has the advantage of showing immediately if the value of  $M$  assumed in (8) exceeds the limit of possible solution, since the maximum value of  $M$  corresponds to the condition  $\log (P'/P'') = 0.217DP/P''$ , very nearly.

As an example of the application of the rule, if we assume  $z_m' = 2.40$  for the second expansion, with  $x = 1.25''$ , and  $P' = 118.4$ , we find from (11)  $DP = 85.79$ ,  $P'' = 82.61$ ,  $\log (P'/P'') = 0.15682$ , and  $0.217DP/P'' = 0.094$ . Equation (1), with  $Z = 2.522$ , and  $aP'V' = 45.58$ , gives  $z_m'' = 2.372$ , showing a difference

$$z_m'' - z_m' = -0.028,$$

which (by the above rule) when multiplied by  $0.094/0.062$ , gives  $-0.042$  to be added to  $2.372$ , leaving  $2.380$ . The final value,  $z_m = 2.380$ , when tested, is found to be correct to the last figure, and gives  $DP = 84.74$ ,  $P'' = 83.66$ , from (11),  $DH = 7.68$  from (2), whence  $DaPV = 1.82$ , and  $aP''V'' = 43.76$ , as required for the initial state in the next expansion.

The results for the several expansions with  $M = 40$  are as follows.

Table III.

H.P. turbine.  $M = 40$ ,  $P' = 167$ ,  $H' = 668$ . State, dry supersaturated.

No.	$\int aVdP$	$z_m$	$DH$	$f$	$DP$	$P''$	$xDP$	$aP''V''$
1	15.98	2.378	7.12	0.446	48.60	118.40	42.5	45.58
2	15.51	2.330	7.68	0.495	34.74	83.66	43.4	43.76
3	15.44	2.309	8.14	0.528	25.34	58.32	44.4	41.86
4	14.47	2.212	8.20	0.566	17.40	40.92	43.5	39.95
5	13.57	2.112	8.15	0.600	12.03	28.89	42.1	38.06
6	11.48	1.902	7.52	0.650	7.68	21.21	38.4	36.92
	86.45	2.205	46.81	0.542	$\Sigma DP = 145.8$	42.38	42.38	10.97

The last line gives the sums and means. The last column gives the values of  $aP''V''$  required in the calculation, and  $DaPV$  for the whole turbine. The small corrections for the difference between  $V_m'$  and  $V_m''$ , and for discontinuity, are here neglected, because they are nearly equal and opposite as explained in the last chapter, § 148.

If the final pressure  $P''$  is given, there is a considerable advantage in working the above method backwards, starting with the last expansion, especially if the flow through the last expansion ap-

proaches the limit of discharge. The final pressure cannot in any case be determined satisfactorily from the mass-flow, because  $M$  is nearly independent of the final pressure, in the majority of practical cases, for a complete turbine. Moreover the rule above given for finding the correct value of  $z_m$  for each expansion from the result of the first trial estimate, works more accurately backwards than forwards. To work the rule backwards, when  $P''$  is given and  $P'$  is sought, it is merely necessary to substitute  $0.217DP/P'$  in place of  $0.217DP/P''$ . This has the advantage that the correction to  $z_m''$  is always smaller than the difference  $z_m'' - z_m'$  instead of larger, so that the work is more accurate. Moreover a considerable error in the estimated value of the final pressure for the whole turbine will make very little difference to the value found for the initial pressure, if the value of  $M$  is nearly right; and the trial value of  $M$ , if uncertain, is readily corrected for small errors by the consideration that it will vary nearly as the square root of  $P'/V'$ .

When the initial and final pressures are observed for each expansion in addition to the mass-flow for the whole turbine, equation (8) serves for determining the probable value of  $(x + 2l)/\tan \alpha$  for each expansion separately, if  $l$  and  $\alpha$  are not assumed to be uniform throughout the turbine. The mean value of  $l$  can be inferred independently from equation (2) if the heat-drop for the whole turbine is known. There will always be a margin of uncertainty in deducing small variations of  $l$  or  $\alpha$  from small differences of pressure observed in experimental tests, but if the calculations are made on a consistent plan, the values found can be employed for deducing the effect of other variations of condition on the assumption that  $l$  and  $\alpha$  remain constant for each expansion, and the results of such calculations will in all probability be of the same order of accuracy as the original observations from which the values of  $l$  and  $\alpha$  were deduced. The chief source of uncertainty arises from change of state of the steam, but as a rule the point at which this occurs will be clearly indicated by the observations. The table shows that the range of variation of  $z_m$  for the separate expansions, which was found to be 2.65 to 1.85 in the absence of leakage, is greatly reduced by assuming  $l = 0.070''$ , and could be further modified by admitting a larger value of  $l$ . But the excessive drop of  $z_m$  in the last expansion is chiefly due to the raising of the final pressure by the auxiliary exhaust and H.P. dummy leakage. The design of the turbine would require a larger expansion ratio

and a much lower final pressure to make  $z_m$  the same for the later as for the earlier expansions. The final pressure in the table, with  $M = 40$  and  $l = 0.070''$ , comes out 21.21, but a small variation in either  $M$  or  $l$  will make a considerable difference in the final pressure. The table gives a good idea of the probable limits of variation of  $z_m$  and  $xDP$  under the conditions assumed, and the effect of small variations of  $M$  or  $l$  is readily estimated without repeating the calculation for the separate expansions.

For example, the rough estimate of  $M$  by the method of the preceding section was made for saturated steam, and would be a little different for supersaturated, as assumed in Table III. But by making due allowance for the variation of  $z_m$  and  $xDP$  as shown in the table, it is possible to estimate the error in  $M$  due to assuming  $z_m$  and  $xDP$  constant. The mean value of  $xDP$  according to the table is 42.88. The mean value assumed in the integral method would be  $x_m \Sigma DP/6 = 42.91$ , which would give  $M = 40.50$  in place of 40. The mean value of  $z_m$  for the same pressure-range would be 2.198, in place of 2.205 as shown in the table, which would increase the error, giving  $M = 40.62$ , as is easily verified by performing the calculation.

The employment of equation (8) in the manner specified for estimating the effect of leakage on the mass-flow, though accurate for one expansion, is necessarily inaccurate for the whole turbine, unless  $z_m$  is the same throughout, as previously explained. It is useful for rough estimates within certain limits, but would be quite inapplicable to a problem involving small differences depending essentially on the variation of  $z_m$ , for example in calculating the small variations of  $M$  due to changes in the final pressure. For this purpose equation (8) must be replaced by XIV (14), as previously shown.

**159. Variation of Final Pressure.** In considering the effect of variation of final pressure on the discharge through a complete turbine, with a pressure-ratio exceeding 4 to 1, it is possible to obtain good results, in spite of the variation of  $z_m$ , without calculating the expansions separately, by employing equation XIV (14), as in the case of a single expansion when the discharge-angle  $\alpha$  is constant. This equation may be put in the form

$$M^2 \Sigma Z'' = M^2 \Sigma (144N \tan^2 \alpha / X^3) = g f_1' \Sigma D(P/V)/(2 - m), \quad (12)$$

which is obtained by adding the equations for the separate ex-

pansions. Since  $m$  is small compared with 2, and does not vary greatly, we may take the mean value

$$m = \log (P'V'/P''V'')/\log (P'/P'')$$

(XIV, § 146) for the whole pressure-range. The sum of the values of the drop of  $P/V$  for all the expansions is simply  $P'/V' - P''/V''$ , the difference of the initial and final values of  $P/V$  for the whole range. The value of the discharge-constant,  $Z'' = 144 \tan^2 \alpha/X^2$ , for each expansion is independent of the speed, and is readily corrected for the effect of leakage on  $M$  by dividing each value of  $Z''$  before addition by the appropriate factor  $(1 + 2l/x)^2$ . The correction for discontinuity of expansion is much less important than in the case of a single expansion with an excessive pressure-range. It will be nearly the same for each expansion under normal conditions, and is easily applied as a final correction to the value of  $M$  by dividing it by the factor  $1 + \log_e r/4\Sigma N$ , where  $\Sigma N$  is the whole number of stages, and  $r$  is the whole expansion-ratio  $V''/V'$ .

As a numerical example of the application of this equation, we may use it to calculate the value of  $M$  for the above H.P. turbine under the conditions assumed in Table III of the last section, with the same final pressure 21.21. From equations (1) and (2) in the usual way we find the following values:

$faVdP = 85.70$ ,  $z_0 = 2.198$ ,  $DH = 47.03$ , whence  $V'' = 16.62$  supersaturated.

$P'/V' = 60.65$ ,  $P''/V'' = 1.28$ ,  $D(P/V) = 59.87$ ,  $m = 0.1288$ ,  $2 - m = 1.8712$ .

The required value of  $\Sigma Z''$ , corrected for leakage with  $l = 0.070''$ , comes out 0.5561, giving  $M'' = 40.2$ . The correction for discontinuity of expansion, with  $V''/V' = 6.04$ , and  $\Sigma N = 72$ , is obtained by dividing  $M''$  by the factor 1.0068, which gives finally  $M = 40.01$ , in agreement with the value  $M = 40$  assumed in calculating the pressure-drop for the expansions separately by means of equation (11).

It will be seen that equations (11) and (12) are exactly consistent when each is employed for its proper purpose. Equation (11) is the most convenient to employ for finding the pressure-drop, etc. in successive expansions when  $M$  is given, but is unsuitable for finding  $M$  for a complete turbine with a large pressure-range unless  $z_m$  happens to be constant. Equation (12) is the most appropriate for the latter purpose, since it does not assume the constancy

of  $z_m$ , and is better adapted to the case of a complete turbine than to that of a single expansion with a large pressure-range.

It follows from equation (12) that the curve representing the variation of  $M$  with increase of  $DP$  for a complete turbine is very similar to that marked 1<sup>a</sup> in Fig. 83, since the correction for discontinuity is small owing to the large number of stages. The variation of  $M$  with change of final pressure will be very small, since  $P''/V''$  is small compared with  $P'/V'$ . Thus if the final pressure in the last example is 28.1 in place of 21.21, we find  $V'' = 15.88$ ,  $P''/V'' = 1.50$ ,  $D(P/V) = 59.15$ ,  $2 - m = 1.869$ , whence  $M = 89.96$  corrected, in place of 40. The discharge becomes practically independent of the final pressure when the expansion ratio is large.

The maximum value of the discharge will evidently vary nearly as the square root of  $P'/V'$ , as in the case of a nozzle, and inversely as the square root of the discharge-constant  $\Sigma Z''$ , corrected for leakage. The curve marked 1<sup>a</sup> in Chap. XIV, Fig. 83, corresponds approximately with the discharge of supersaturated steam through a H.P. turbine with initial state  $P' = 164.7$  lbs. abs. dry saturated, and with a discharge-constant  $\Sigma Z'' = (12 \tan \alpha/100)^2 = 0.1087$ , if  $f_1' = 1$ , or 0.0960 for  $f_1' = 0.888$ , as assumed in the last example. Taking the maximum ordinate of the curve as 96.5, and omitting  $\sqrt{N}$  which is included in  $Z''$ , the maximum discharge for  $\Sigma Z'' = 0.556$  would be 40.1 lbs./sec. at  $P' = 164.7$ , or 40.6 at  $P' = 167$  lbs. But the actual value will also depend to some extent on the state of the steam, and on the speed, in so far as the conditions affect the values of  $V''$  and  $m$ . Thus  $V''$  will be smaller and  $m$  larger for supersaturated than for saturated steam. The reduction of  $m$ , as shown by equation (12), will tend to reduce the values of  $M$  for saturated steam as compared with the values given by the curve, which is drawn for dry supersaturated.

By way of comparison we may calculate the flow through the same H.P. turbine in the case of *saturated* steam, taking the same conditions as in Table III with the final pressure 21.21. Equations (1) and (2) give the data: mean  $z_m = 2.244$ ,  $\Sigma DH = 48.8$ ,  $2 - m = 1.9142$ ,  $V'' = 18.16$ ,  $D(P/V) = 59.48$ . Substituting these values in equation (12) we find  $M = 89.60$  corrected.

Having found the flow, it would be possible to calculate the expansions in succession, as in Table III, by way of verification, using equations (1), (2), and (8). But the calculation is more troublesome in the case of saturated steam than in the case of dry steam, owing to the necessity of continual reference to the

tables and of interpolation for finding the volume of the wet steam from the heat-drop. For this reason, among others, the following method is preferable in point of expedition, and is sufficiently accurate for all practical purposes, besides being most instructive as an independent method of calculation for the separate expansions.

It is evident from equation (12) that the drop of  $P/V$  in each expansion is proportional to the value of the discharge-constant  $Z''$  for the expansion considered. The drop of  $P/V$  is proportional to the drop of  $P^{2-m}$ , which is easily calculated for each expansion by dividing the difference between the initial and final values of  $P^{2-m}$  in the same proportion as the separate values of  $Z''$  bear to their sum. With the values above given of  $P'$ ,  $P''$ , and  $2 - m$ , we have  $P'^{2-m} = 17978$ ,  $P''^{2-m} = 346.2$ , difference 17632. Each value of  $Z''$  has to be multiplied by the ratio 17632/0.5561 to find the corresponding value of the drop of  $P^{2-m}$ , as in the following table.

Table IV.

H.P. turbine. Saturated steam.  $H' = 668$ ,  $P' = 167$ ,  $P'' = 21.21$ .

Expansion No.	1	2	3	4	5	6
$Z''$ ( $l = 0.070''$ )	0.27040	0.14264	0.07605	0.03813	0.01950	0.00938
$D(P^{2-m})$	8574	4522	2411	1209	618.3	297.5
$P^{2-m}$	17978	9404	4882	2471	1262	643.7
Log $P^{2-m}$	4.2547	3.9733	3.6886	3.3929	3.1011	2.8087
Log $P$	2.2227	2.0757	1.9269	1.7724	1.6200	1.4673
$P$	167.0	119.04	84.51	59.21	41.69	29.33
$DP$	47.96	34.53	25.30	17.52	12.36	8.12
$z_m$	2.369	2.336	2.328	2.251	2.190	2.032
$DH$	7.09	7.70	8.23	8.38	8.54	8.22

The values of  $P^{2-m}$  are obtained from the differences given in the third line of the table by adding the final value 346.2 to the drop 297.5 in the sixth expansion, giving 643.7 at the end of the fifth, and so on. The values of  $P$  at the intermediate points between the expansions are found by taking the logs of  $P^{2-m}$ , dividing by  $2 - m$  (with a Fuller slide-rule), and taking the antilogs. The pressure-drop  $DP$  for each expansion is obtained by taking differences, and the required values of  $z_m$  and  $DH$  are then easily found from equations (8) and (2) respectively, with the leakage factors  $x + 2l$ , and  $1 - 8l/x$ . The numerical value of the constant in (8) or (11) is 20.54, for saturated steam, in place of 20.75 for supersaturated, being simply proportional to  $M$ . As a rough verification of the

accuracy of the method, the sum of the values of  $DH$  comes out 48.2, in place of 48.8 as calculated from the initial and final pressures.

It will be seen that, when the blade-heights are in an ascending geometrical progression with a common ratio  $\sqrt[3]{2}$ , the corresponding values of  $Z''$  form a descending geometrical progression with a common ratio  $1/2$ , to a similar degree of approximation. The value of  $Z''$  for the first expansion is nearly as large as the sum of the remainder, and is the most important in determining the discharge. The value of  $M$  for saturated steam is only 1 per cent. less than for supersaturated, because the volumes are nearly the same in the first expansion, as previously remarked. The reduction is mainly due to the reduction of  $m$  from 0.0938 supersaturated, to 0.0838 saturated. The fall of  $z_m$  in the last two expansions is less pronounced in the case of saturated steam ( $S$ ) than in Table III for supersaturated ( $SS$ ), because the final volume in Table IV is increased from 16.62  $SS$  to 18.16  $S$ , and the expansion ratio from 6.55 to 6.6  $S$ . The design of this particular turbine would require a pressure-ratio of 10/1, or an expansion ratio of 8.22, in the case of saturated steam, to make the value of  $z_m$  approximately the same for all the expansions with the leakage correction above assumed. It is very likely that the H.P. turbine was designed to suit a pressure-range from 165 to 16.5 lbs. abs., with 16 lbs. to 1.6 for the L.P., but the conditions of the full-speed trials would correspond to an overload, with more work on the L.P.

**160. Maximum Discharge and Power.** When the final pressure is reduced, keeping the initial pressure constant, the value of  $M$  will approach a maximum, which is finally reached when the velocity of exit from the last ring of blades is that of sound. If the final pressure is reduced beyond this point there is no further increase in the discharge or the power. The value of  $M$  reaches the limit very gradually and continuously as previously indicated, but the power increases with pressure-drop at a nearly uniform rate right up to the limit, at which point the increase terminates abruptly. The point at which the limit is reached is beyond the practical range, but the limit is of practical interest in relation to the character of the power curve as affected by variation of final pressure.

If we eliminate  $z_m''$  between equations (2) and (8), we obtain the power  $M''DH$  (omitting the constant for reduction to horsepower), for each expansion,

$$M''DH = [2kDP - M''/(x + 2l)](x - l)Z, \dots, (18)$$

in which  $k$  represents the constant  $720gf_1/NR \tan \alpha$ . This equation shows that the power for each expansion is nearly a linear function of the pressure-drop  $DP$  when  $M$  is approaching the maximum. The power for the complete turbine will also maintain approximately a linear character in relation to the pressure-drop, up to the limit at which it ceases to increase with further drop of pressure, provided that the speed remains constant.

As the limit is approached, the steam-velocity increases rapidly in the last expansion with a high value of  $z_m$ , so that the heat-drop for the whole turbine cannot be found accurately by assuming  $z_m$  constant. It is possible however to find accurate values, even at the extreme limit, by calculating the pressure-drop and  $z_m$  for each expansion as in § 159, by the last method described. The limiting value of  $M$  is first estimated from equation (12) with any convenient low value of the final pressure. The application of condition XIV (11), for the velocity of sound at the last blade-ring, will then give a fairly accurate value of the final pressure at the limit. With this value of the final pressure, the values of  $P^{2-m}$  at intermediate points are readily found, and the values of  $DP$ ,  $z_m''$  and  $DH$  for the separate expansions are deduced as in Table IV. The sum of the values of  $DH$  gives the required total heat-drop at the limit with considerable accuracy.

To find the critical value of the final pressure for the H.P. turbine in the last example at 822 revs./min. in the case of saturated steam, we have the limiting value of  $M$ , 89.95, as previously calculated. The value of  $X'$  in equation XIV (11) is

$$(X - 78ml) \cos \alpha + 78ml = 403.5 \text{ sq. in.,}$$

corrected for tip-leakage. The equation (11) gives  $P''/V'' = 0.0888$ , whence  $P'' = 3.87$ , if  $2 - m = 1.919$ . The value  $P'' = 3.4$  will be a sufficient approximation for the present purpose.

The following table gives the values of  $M$ , and of the total heat-drop  $\Sigma DH$  for different values of the final pressure  $P''$ . The values in the second column headed  $M''$  are those given by equation (12), corrected for leakage, but with the correction for discontinuity omitted, as required in calculating  $z_m''$  from  $DP$ . The correction of  $M$  for discontinuity is small, ranging from 0.26 at 8.4 lbs. to 0.28 at 50 lbs., depending chiefly on the first expansion which is little affected by the final pressure. The table also gives the values of  $z_m''$  for each expansion separately to illustrate the effect of the variation of  $P''$ , which is greatest in the last expansion. The value of  $\Sigma DH$ ,



calculated from the mean value of  $z_m$  for the whole turbine by equation XIV (1 a), agrees very closely with that found from the sum of the separate expansions at  $P'' = 16$  when  $z_m$  is nearly the same throughout, but would be about 6 per cent. too large at  $P'' = 8.4$  and at 50, owing to the variation of  $z_m$  which is assumed constant in (1 a).

Table V.

H.P. turbine. Variation of final pressure. Saturated steam.

$P''$	$M''$	$\Sigma DH$	$z_1$	$z_2$	$z_3$	$z_4$	$z_5$	$z_6$
3.4	40.20	64.79	2.385	2.378	2.428	2.483	2.740	4.153
10	40.14	57.83	2.380	2.365	2.408	2.428	2.587	3.083
16	40.00	52.41	2.369	2.343	2.364	2.335	2.374	2.421
23	39.80	47.12	2.351	2.308	2.296	2.205	2.106	1.905
30	39.52	42.61	2.330	2.264	2.206	2.053	1.863	1.555
40	38.97	37.17	2.282	2.187	2.071	1.841	1.572	1.219
50	38.27	32.45	2.229	2.092	1.919	1.643	1.331	0.989

The values of  $DP$  for the separate expansions are readily found from those of  $z$  by equation (8)  $(x + 2l) DP = 0.5188 M'' z_m''$ . In finding the separate values of  $DH$  from those of  $z$ , the expression for  $f''$  in equation (2) has been taken as  $(x - l)/(x + 2l)$ , with  $l = 0.070''$ , giving for  $Zf''$  the series of values 1.979, 2.141, 2.274, 2.406, 2.538, 2.687, at 322 revs.

The curves in the annexed Fig. 84 illustrate the variation of (1) the horse-power,  $H.P. = M \Sigma DH / 0.3928$ , (2) the mass-flow  $M$ , (3) the relative efficiency  $F$ , and (4) the consumption,  $C = 1414 / \Sigma DH$  in lbs. per horse-power hour, each being plotted against the final pressure  $P''$ , in lbs./sq. in. abs., at a constant speed of 822 revs./min., with initial state  $P' = 167$  lbs. abs., and  $H' = 668$ . The relative efficiency  $F_1$  is given in per cent. by the scale on the left, which also serves for  $M$  in lbs./sec. The H.P. ranges from 8142 to 6588, and is given by the same scale multiplied by 100. The consumption  $C_1$  ranges from 21.82 lbs. per H.P.H. at  $P'' = 3.4$  lbs., to 48.57 at  $P'' = 50$  lbs., and is shown by the scale on the right. The curves  $F_2$  and  $C_2$  refer to the same case when the speed is doubled, the other conditions remaining unaltered. These curves have been shifted relatively to  $F_1$  and  $C_1$  to facilitate comparison. The values of  $F_2$  as read by the scale on the left must be increased by 20 per cent., and those of  $C_2$  read as by the scale on the right must be reduced by 10 lbs.

The curve representing  $M$  approaches the limit at  $P'' = 8.4$  lbs.

very gradually, as previously explained, but that representing the H.P. continues to rise at an increasing rate up to the limit, after which the H.P. remains constant. The curve representing  $F_1$  shows a rapid fall at low pressures and a marked increase for high values of  $P''$ , tending to a maximum in the neighbourhood of  $P'' = 70$ , beyond the range of the figure, and falling again at higher pressures to zero when  $DP$  is very small.

The "theoretical value" of the consumption  $C$  is often estimated from the adiabatic heat-drop by assuming a constant value of  $F$ . The effect of this is shown by the broken curve marked Th, taking the actual value of  $F_1$  at 16 lbs. as the constant required. Owing to

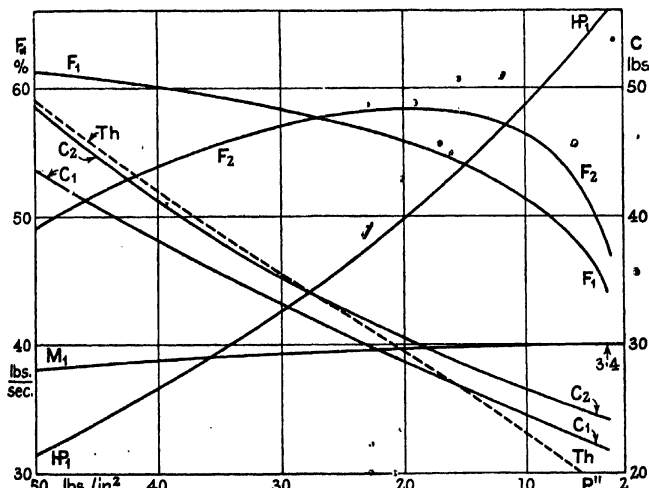


Fig. 34. H.P. Turbine. Variation of  $C$ ,  $F$ ,  $M$ , and  $HP$  with final  $P$ .

the wide range of variation of  $F$  with final pressure, this method is of little practical use. It makes the correction of  $C$  for variation of final pressure about 60 per cent. too large in the present instance. When the speed is doubled, the maximum of  $F$ , as shown by the curve  $F_3$ , occurs at a much lower pressure, near 20 lbs., but the final drop of  $F$  is still strongly marked. The curves  $F_1$ ,  $F_2$ , represent extreme cases. They are of interest chiefly as an illustration of the futility of assuming  $F$  constant in cases of this kind.

**161. Correction of Consumption for Change of Pressure.** The performance of a steam-engine or turbine is commonly

stated in terms of the consumption of steam in lbs. per horse-power-hour, or other convenient units. The value of the consumption  $C$  is inversely proportional to the actual heat-drop  $DH$ , or to the adiabatic heat-drop  $DH_a$  multiplied by the relative efficiency  $F$ .

$$C = k/DH = k/DH_a \times F. \dots\dots\dots(14)$$

The values of the constant  $k$  most commonly required in different systems of units are shown in the following table.

$C$ in lbs. per horse-power-hour	= $1414.3/DH$ (cals. C.)	= $2546/DH$ (B.Th.U.)
$C$ in lbs. per kilowatt-hour	= $1895.5/DH$ „	= $3412/DH$ „
$C$ in kg. per cheval-vapeur-heure	= $632.4/DH$ „	= $1138/DH$ „
$C$ in kg. per kilowatt-hour.	= $860.0/DH$ „	= $1548/DH$ „

When the correction to the consumption for change of vacuum is stated or required in terms of cms. or inches of mercury, the following reduction factors may be employed to reduce the readings of the vacuum-gauge to lbs. per sq. in., or kg. per sq. cm., as required in the (F.P.C. or F.) and (K.M.C.) systems of units:

$$\begin{aligned} 1 \text{ inch of mercury} &= 0.4910 \text{ lb./sq. in.} = 0.08452 \text{ kg./sq. cm.} \\ 1 \text{ centimetre} &,, = 0.1933 \text{ lb./sq. in.} = 0.01359 \text{ kg./sq. cm.} \end{aligned}$$

When it is required to calculate the changes of consumption for any given machine over wide ranges of variation of pressure, or superheat, or speed, the values of  $C$  should be deduced from those of  $DH$  calculated by the method explained in the preceding section, which will give fairly accurate results for any practical changes in the conditions from quarter load to 50 per cent. overload, or half speed to double speed, provided that there is no change in the state of the steam. But if sufficient data are available, or if the state changes from dry to wet in the course of the expansion, or if there is a change of  $M$ , it may often be desirable to calculate some of the expansions separately. On the other hand, in the case of small changes of conditions such as often occur in full-load tests, a much simpler method of calculation will suffice for practical requirements.

The correction most often required in practice is the percentage change of consumption per unit change (1 lb./sq. in. or 1 in. vacuum) of final pressure, when the conditions deviate slightly from the normal value of the final pressure for which the machine was designed. Assuming that the normal pressure range is defined as that which makes the value of  $x_m$  nearly the same for all the expansions, a general expression for the percentage correction of the consumption for change of final pressure at constant speed,

is readily deduced from equations (1) and (2), and will apply with considerable accuracy to any kind of turbine, with any initial state or speed-ratio, provided only that the value of  $z_m$  is nearly uniform.

If we differentiate equations (1) and (2) with respect to  $P''$ , and divide the differential of (2) by that of (1) to eliminate  $dz/dP''$ , we find an expression for  $dDH/dP''$ , or  $(DH/C)(dC/dP'')$ , which reduces to the form

$$\begin{aligned} (100/C)(dC/dP'') &= - (100/DH)(dDH/dP'') \\ &= 100V''z_0/(2z_0 - 1) V_m' DP. \dots (15) \end{aligned}$$

The expression on the left represents the required *percentage* correction to  $C$ , which is the same as the percentage correction to  $DH$ , but opposite in sign, because  $C$  varies inversely as  $DH$ . Of the quantities in the expression on the right,  $V''$  is the final volume,  $V_m' DP$  is the integral of  $VdP$ , and  $z_0$  is the mean value of  $z_m$  for the whole turbine as obtained from equations (1) and (2) by the usual method under normal conditions when  $z_m$  is nearly uniform.

Since the form of the curves in the last figure shows that the percentage correction to  $C$  per unit drop of final pressure is nearly constant up to the limit, the value given by the above expression will apply through a wide range, although the value of  $z_0$  is applicable to normal conditions only, and would not give  $DH$  or  $C$  very accurately at other points. The form of the expression shows that the percentage correction will increase as  $z_0$  diminishes and the speed increases, but the consumption is reduced by diminution of  $z$  over the usual range from  $z = 2.4$  to  $z = 1.2$ , so that the consumption curves remain nearly parallel (as shown in the Fig. 84) when the speed is changed, although the *percentage* corrections are different. The same expression is applicable to the *vacuum-correction* of any turbine, but it is necessary to insert a numerical factor to reduce  $DP$  to inches or cms. of mercury, if the correction is to be expressed in terms of mercury.

The percentage correction of the consumption for change of *initial* pressure may be obtained in the same way as that for final pressure, and is given by the same expression, with the initial pressure  $P'$  in place of the final pressure  $P''$ , and the initial volume  $V'$  in place of the final volume  $V''$ . The sign of the correction for initial pressure is negative because an increase of initial pressure tends to reduce the consumption. The correction per 1 lb. change of initial pressure is *smaller* than that for final pressure in the ratio

of  $V'$  to  $V''$ , and is seldom required in practice, because the initial pressure is usually adjusted to some specified value. The correction for 1 per cent. change of initial pressure is obtained by multiplying the correction per lb. by  $P'/100$ , and is *greater* than the correction for 1 per cent. change of final pressure in the ratio of  $P'V'$  to  $P''V''$ . If both initial and final pressures are increased by 1 per cent., keeping the ratio  $P'/P''$  constant, the percentage reduction of consumption will be  $(P''V'' - P'V') z_0 / (2z_0 - 1) V_m' DP$ , which reduces to the form  $-mz_0 / (2z_0 - 1)$ , since  $V_m' DP = D(PV)/m$ .

The effect of increase of initial pressure on the pressure distribution is similar to that of reduction of final pressure in that both tend to increase  $DP$  and  $z_m$  in the last expansion. The effect on the last expansion is the most important, as previously illustrated, and is taken into account in the formula for the consumption-correction by the implied condition that the value of  $z_m$  for the last expansion must be the same as the mean value  $z_0$  for the whole turbine assumed in using the formula. The fulfilment of this condition is readily tested in any actual trial by observing the pressure-drop  $DP$  on the last expansion, which, according to equation (8), if  $z_m$  is constant, must be the same fraction of the whole pressure-drop  $\Sigma DP$  as the last expansion-constant,  $Z' = Nu \tan \alpha / X$ , is of the sum  $\Sigma Z'$ . The value of the fraction  $z_0 / (2z_0 - 1)$  varies from  $3/4$  when  $z_0 = 1.5$ , to  $2/3$  when  $z_0 = 2$ , and diminishes with increase of  $z_0$  to a limit  $1/2$  when  $z_0$  is very large. The correction also varies inversely as the available energy  $aV_m' DP$ , which is roughly twice as great for a high-pressure *condensing* turbine as for a low-pressure turbine, or for a high-pressure non-condensing turbine. It also depends on the final volume  $V''$  for which the machine is designed, so that it is very useful to have a simple formula including all the conditions.

As a numerical example of the application of the correction, we may take the case of the H.P. non-condensing turbine for which the consumption curves  $C_1$  and  $C_2$  in the last figure have already been calculated by a different method. For graphic illustration of a particular case, it appears best to plot the curves as already shown against the final pressure, but in comparing results it is more convenient to state the effect of a given *percentage* change in the pressure, since the numerical values of the percentage correction are in that case more nearly of the same order of magnitude at different pressures. This method of expression is accordingly adopted in the following table, in which  $C_0$  represents the con-

sumption calculated for the normal range with final pressure  $P''$  starting in each case from  $P' = 167$  lbs. abs.

Table VI. Consumption Correction percentage of  $C_0$  for 5 per cent. change of pressure.

Initial state			Results for Normal Range							Correction for 5 % of $P$		
	$H'$	$V'$	$P_0''$	$V_0''$	$V_m' DP$	$z_0$	$\delta$	$C_0$		Initial	Final	Diff.
Dry	668	2.785	16	21.51	919	2.307	27.82		1.62%	1.20%	0.42%	
$C_1$ sat.	668	2.785	16	23.62	979	2.382	26.98		1.50%	1.22%	0.28%	
$SH$	770	4.123	16	33.56	1432	2.880	21.35		1.45%	1.13%	0.32%	
$C_2$ sat.	668	2.785	15	23.88	980	1.191	18.38		2.10%	1.57%	0.53%	

The state assumed for the first line is dry supersaturated throughout the expansion. For the second line the usual state of saturation is assumed, as in the calculation of the curve marked  $C_1$  in the last figure. For the third line ( $SH$ ) superheated, the initial temperature is  $195^\circ \text{C}$ , or  $350^\circ \text{F}$ , and the steam remains superheated throughout, but the superheat makes little change in the pressure-distribution, which is intermediate between 1 and 2. The last line corresponds to the curve  $C_2$  with saturated steam at double speed. This requires a lower value of the final pressure,  $P_0'' = 15$ , to give a nearly uniform value of  $z_m$ , equal to half the value of  $z_0$  for  $C_1$ . The increase in the correction for this case as compared with  $C_1$  is due to the change of  $z_0$ . The values of the correction given by the formula (15) for a range of 50 per cent. on either side of  $P_0''$ , e.g. from 24 to 8 lbs. in the case of  $C_1$ , agree so closely with the curves that they could not be distinguished on the scale of the figure. The extent of range covered is a great practical advantage in applying the method.

The reason why the simple formula for the slope of the consumption curve  $dC/dP''$  at the normal value of the final pressure  $P_0''$  gives so good an approximation to the correction through a wide range, is that the consumption curve is nearly straight in this region. It appears best for this reason to correct the value of the consumption itself directly for change of final pressure, and to deduce the corresponding value of the relative efficiency  $F$  from the corrected value of  $C$ , in place of attempting to calculate  $C$  from the theoretical value of  $F$ . The normal pressure-ratio for a given machine varies little with other conditions of running, and is readily deduced from the dimensions. Knowing the appropriate pressure-ratio and the initial pressure, an approximate value of

$P_0''$  is obtained, which will usually suffice for calculating the consumption correction, the error of which will be only about a quarter of the percentage error in the value of  $P_0''$  assumed.

The correction for initial pressure is seldom required in practice, and will not apply for such large percentage changes as the correction for final pressure, because the consumption curve, when plotted against changes of initial pressure is necessarily far from being of uniform slope. Moreover the correction for initial pressure will depend on changes of initial state. The values of this correction given in the preceding table are those obtained on the assumption that the final state remains constant when the initial pressure is changed, which is seldom the case in practice. Thus if the initial pressure is changed under the condition that the initial state remains dry saturated, or that the initial value of  $H$  remains constant, as in regulation by throttling, the corrections will be somewhat smaller than those given in the table, and there will be some change in the final state even if the final pressure is kept constant. It is often assumed that there will be no change in the consumption if the initial and final pressures are changed in the same ratio. This will not be strictly accurate, even if the initial value of  $H$  remains constant, if the state of saturation is assumed for the expansion. But the difference between the initial and final corrections will be relatively small if  $H'$  is constant, and the increase of super-saturation loss with initial pressure may suffice to compensate for the residual error in practice.

**162. Vacuum Correction for Consumption.** In practice the correction of the consumption for changes in the vacuum is the commonest case, for which a considerable volume of experimental evidence is available by way of verification of the formula. The curves in the annexed Fig. 35 were drawn in the same way as those in the preceding figure, for the case of a complete turbine H.P. and L.P. of the *Mauretania*, expanding from 165 lbs. abs. (dry sat.) to 1 lb. sat., but the pressure scale has been altered to read vacuum in inches of mercury, bar. 30". The scales of C and F have also been changed to read *percentage* of the normal C and F at  $P_0'' = 1$  lb. The scale of HP is arbitrary, taking 115 to represent the normal HP. The curve Th is the "theoretical" consumption obtained by taking F constant.

The formula for the percentage change of the consumption, with  $x_0 = 2.0$ ,  $aP_0''V_0'' = 80.8$ , and  $\int aVdP = 195$ , gives a rate of

change of  $C$  equal to 5.1 per cent. per in. of vacuum, which agrees with the slope of the tangent to the curve at 1 lb., and would give good results for a change of 50 per cent. either way in the final pressure, from 27 to 29" vacuum. But for large changes of pressure, e.g. for 22" vacuum, it would be necessary to use the curves obtained by the previous method, § 160, as shown in the figure.

If we take the case of a turbine expanding from 180 lbs. gauge, with a superheat of 150° F., to 28" vac. (bar. 80"), which is often

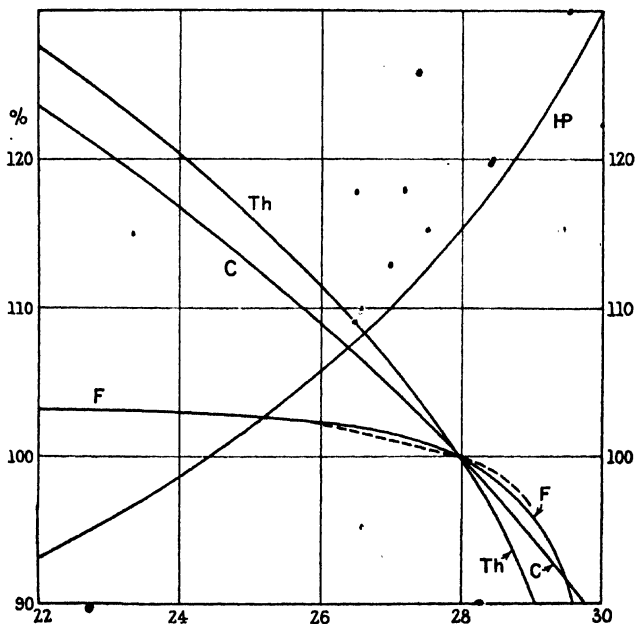


Fig. 35. Vacuum Correction for  $C$ ,  $F$ , and  $HP$ .

taken as the standard for a H.P. condensing turbine, and assume  $z_0 = 1.56$  for a reaction turbine, equivalent to 8.12 for an impulse turbine, we obtain very similar curves with the same rate of change of  $C$  at 28" vac. In applying the formula to the impulse turbine it is merely necessary to put  $2z - 2$  in the denominator in place of  $2z - 1$ . The values of the fraction  $z/(2z - 2)$  for the impulse turbine are the same as those of  $z/(2z - 1)$  for the reaction turbine, if the values of  $z$  for the impulse turbine are twice as great as the corresponding values for the reaction turbine. It is natural that the



same type of formula should apply to both types of turbine, because, apart from the form of the moving blades, of which account is taken by the substitution of  $2z - 2$  for  $2z - 1$ , the conditions of flow are very similar in the final stages, as previously explained in Chapter XI, § 127. In fact, the theory here proposed gives remarkably good agreement with the results of experiment.

The experimental curves given by K. Baumann (*Journ. Inst. Elect. Eng.*, No. 218, vol. 48, p. 828, 1912) have been generally accepted as fairly representing results obtained in average practice, and as applying to reaction turbines as well as to impulse turbines. The curve given by Baumann as representing the vacuum correction of an impulse turbine designed for 28" vacuum with initial pressure 180 lbs. gauge and superheat 150° F., extends only from 26" to 29", but could not be distinguished between these limits from the curve shown in Fig. 35. His curve for the corresponding variation of  $F$ , deduced from that of  $C$ , is indicated by the broken line in the figure, which is straight between 26" and 28" but shows a rapidly increasing fall to 29". It is evident, however, that the value of  $F$  should approach a maximum somewhere in the neighbourhood of 24", and that the variation cannot therefore be represented satisfactorily by a straight line between 26" and 28". The values of the vacuum-correction for consumption given by the British Thomson Houston Company are of the same general character, but somewhat larger than those given by Baumann, in the case of high-pressure condensing turbines.

In the case of low-pressure turbines, the same formula applies, but the percentage correction is much larger for the same final state and speed-ratio owing to the smaller value of the available energy. Taking the standard case as that of a turbine expanding from an initial pressure of 16 lbs. abs. (dry sat.) to a vacuum of 27.5" (bar. 30"), the consumption correction curve comes out very nearly a straight line between 26" and 29" with a slope of 10.3 per cent. of the consumption at 27.5" for each 1" change of vacuum. The curve given by Baumann for the same case is also practically straight, but shows a slope of nearly 18 per cent., whereas the B.T.H. curve for this case gives very close agreement with the formula here proposed. The discrepancy could no doubt be explained if more precise details were available. The vacuum correction for a low-pressure turbine is so large that a good deal depends on the exact meaning of the phrase "designed for the vacuum," and on the exact manner in which the correction is stated. Thus 18 per

cent. of the consumption at 27.5" vac. is equivalent to 11.5 per cent. of the consumption at 26.5" vac. or to 14.5 per cent. of the consumption at 28.5" vac.

It will be seen that the expressions above given for the effect of change of initial or final pressure, and for the vacuum-correction, depend essentially on the relation between the available energy and the heat-drop implied by the fundamental equations (1) and (2) at the beginning of the chapter, and on the corresponding variation of the kinetic efficiency with the velocity-ratio. This has already been roughly verified by the consideration that the flow is nearly independent of the speed, and by the form of the efficiency curves given in Chapter XI, Fig. 29. The agreement of the calculation with the experimental curves for the vacuum-correction, affords further confirmation of a less direct character, but equally satisfactory so far as it goes.

Additional evidence may be obtained by calculating the heat-drop and power in a similar way for other variations of condition. Thus if we calculate the variation of power at constant speed for a reaction turbine, when regulated by throttling down to the minimum output, which is easily done by the method of § 159, we can plot the power against the total consumption as in Fig. 28. The result is a most remarkable approximation to a straight line, as found by experiment, and gives a very close estimate of the steam required even at no load. The heat-drop becomes negative in the later expansions at no load, and involves such extreme variations of  $z$  that the calculation affords a fairly severe test of the theory. If the speed is maintained constant while the steam is reduced *below* that required for no load, the curve returns to the origin after a short excursion into the negative region. But for very low loads the effects are so peculiar that it is necessary to calculate the last few expansions separately.

The effect of change of speed on the power is easier to calculate, because it does not greatly affect the pressure distribution. The results appear to agree with experiment, but cannot be tested through so wide a range, and require correction at high speeds for the effect of fan-action, as estimated by the formula of § 129, which is necessarily uncertain. They appear to indicate that the speed attainable by a reaction turbine, if the machine runs away, cannot exceed a limit corresponding to the value  $z = 1/2$  for the velocity-ratio, and should in fact be appreciably less.

## CHAPTER XVI

### THE PRESSURE DISTRIBUTION IN A REACTION TURBINE

**163. Observations of the Pressure Distribution.** The quantities most commonly observed or estimated in an experimental test are, the initial and final pressures, the steam consumption, the revolutions, and the shaft-horse-power. If the steam supply is superheated, the initial superheat is also required for estimating the relative efficiency. But for a theoretical investigation of the conditions of flow, especially when the load is varied or the conditions of running deviate from the normal, it is most important to take observations at intermediate points in addition to the initial and final states. The pressure is the easiest quantity to observe, and is capable of affording the most useful information with regard to the state of the steam and the efficiency of the several stages of the expansion. Observations of the temperature are more difficult, but would be useful for determining the state of the steam in the early stages of superheat. It would also be theoretically possible to measure the actual value of  $H$  at any stage, but this is so difficult that it has never been attempted.

The object of the present chapter is to show how the observation of the pressure distribution at suitable points may be utilised to throw light on the state of the steam and the conditions of flow, when the dimensions and speed are known. Since the object is mainly to illustrate general principles and methods of calculation depending on the properties of steam, and since reliable experimental data are so scarce as to be almost non-existent, in order to avoid endless repetition of numerical details of dimensions and to facilitate comparison of different methods, the results will all be worked out for a particular turbine. But the same methods may be applied without difficulty to any other case by simply changing the numerical values of the constants for the turbine.

As an example of the application of the methods in question, we will take first one of the high-pressure turbines of the *Mauretania* for which fairly complete details are available. A special

reason for selecting this example is that the turbines were of large size and slow speed, so that the effects of tip-leakage and supersaturation might be expected to be relatively small. If the effects of supersaturation can be demonstrated in such a case, we should reasonably infer that they will be at least equally important in the case of high-speed machines.

The following are the material dimensions of the H.P. turbine. Diameter of rotor, 96 inches, with eight expansions. The numbers of stages  $N$  in the separate expansions are variously given by different authorities. The numbers given in the following table have been verified by counting the rows on a photograph of the H.P. rotor. The blade-heights are quoted as ranging from  $2\frac{1}{2}$  to  $12\frac{3}{8}$  in., with a common ratio 1.24. The values for the intermediate expansions are calculated to the nearest eighth of an inch, and are taken as representing the radial dimension  $x$  of the annular area  $X$  between rotor and casing for each expansion. The actual blade-heights would be less than  $x$  by the clearance  $l$ . The annular area

$$X = \pi x (96 + x) \text{ sq. in.}$$

Table I. Dimensions of H.P. turbine of SS. *Mauretania*.

Expansion No.	1	2	3	4	5	6	7	8
No. of stages, $N$	16	16	16	16	14	15	15	15
Blade-height, $z$ in.	$2\frac{1}{2}$	$3\frac{1}{8}$	$4\frac{1}{4}$	$5\frac{1}{2}$	$6\frac{1}{2}$	8	10	$12\frac{3}{8}$
Annular area, $X$ in. <sup>2</sup>	853	1054	1338	1670	2093	2614	3330	4213

The following values of the expansion constants,  $Z$ ,  $Z'$ , and  $Z''$ , are calculated from the above table at 194 revs. for comparison with the observations on the pressure-distribution at the same speed.

Table II.

Expansion constants at 194 revs., corrected for leakage,  $l = 0.1''$ .

No.	1	2	3	4	5	6	7	8	Sums
$Z$ cals.	2.480	2.511	2.555	2.606	2.337	2.578	2.678	2.800	20.544
$Zf''$ "	2.228	2.300	2.383	2.463	2.232	2.483	2.509	2.733	19.421
$Z'$ "	4.015	3.313	2.662	2.173	1.547	1.354	1.079	0.883	17.026
$Z'' \times 10^6$	2077	1396	885.6	579.0	327.0	227.2	141.3	89.0	5721.6

Formulae:  $Z = Nu^2/Jg$ ,  $Z' = Nu \tan \alpha/X$ ,  $Z'' = aZ^2/gZ$ , in F.P.C. units.

The mean blade velocity  $u$  may be taken as  $RX/720x$ , where  $R$  is the speed in revs./min. The assumption  $\alpha = 70^\circ$  ( $\beta = 20^\circ$ ) for

the discharge angle appears to agree fairly with the observed value of the mass-flow, if the efficiency constant  $f_1'$  in XIV (1) is taken as 0.888. The blade-angle is assumed to be uniform, with normal blades throughout the turbine.

The energy constant  $Z$  is proportional to the available energy in each expansion when  $z_m$  is the same for the different expansions. The product  $f'Z$  is similarly proportional to the heat-drop. The factor  $f'$  is taken as  $(x - 0.1)/(x + 0.2)$ , with the clearance  $l = 0.1$  in., as explained in § 157, to allow for the effect of tip-leakage.

The expansion constant  $Z'$  is proportional to the pressure-drop  $DP$  in each expansion, when  $M$  and  $z_m$  are the same for the different expansions.

The discharge constant  $Z''$  is independent of  $z_m$  and  $u$ , and is proportional to the drop of  $P/V$  in each expansion when  $M$  is uniform throughout.

The following pressure readings were taken at the points intermediate between the expansions during the full-power trials of the *Mauretania* at a mean speed of 194 revs./min., on both H.P. and L.P. turbines.

Table III.

	H.P. Turbine	L.P. Turbine
Receiver pressure	150 lbs./in. <sup>2</sup> (gauge)	5 lbs./in. <sup>2</sup> (gauge)
End of first expansion	113 " "	0 " "
" second "	87½ " "	4 in. vacuum "
" third "	63 " "	10½ " "
" fourth "	43 " "	16½ " "
" fifth "	31½ " "	21½ " "
" sixth "	21½ " "	24 " "
" seventh "	13 " "	26 " "

Vacuum in condenser, 28 in. Barometer, 30 in.

The low-pressure readings are naturally somewhat uncertain, but special arrangements had been made for taking readings at the various points in rapid succession, and the readings are said to have been extremely steady. Those for each turbine were taken on the same indicator, so that the drop of  $P$  for each expansion would probably be free from zero errors, but the receiver pressures appear to have been taken on different gauges.

**164. Theoretical Formulæ for the Intermediate Pressures.** It has frequently been remarked that the absolute

pressures observed in the H.P. turbine of the *Mauretania* on this occasion follow approximately a geometrical progression with the same common ratio as that of the blade-heights in successive expansions. This is often quoted as the "law of pressure-distribution" in a reaction turbine of this type, but is not very accurate in the present instance. The common pressure-ratio from the initial and final pressures comes out 1.304, whereas the common ratio of blade-heights is 1.24, and the intermediate values of  $P$  show a systematic deviation, as illustrated in the following table.

Table IV.

Absolute pressures calculated as a geometrical progression.

End of Expansion No.	1	2	3	4	5	6	7.
Observed pressure, abs.	127.7	102.2	77.7	57.7	46.2	36.2	27.7
Calculated as G.P.	126.3	96.8	74.2	56.9	43.6	33.5	25.7
Diff. (obs. - calc.)	+ 1.4	+ 5.4	+ 3.5	+ 0.8	+ 2.6	+ 2.7	+ 2.0

The sum of the differences comes to 18.4, and would be further increased if allowance were made for receiver-drop from the H.P. receiver to the first row of blades. The "Law" as commonly stated has no physical interpretation, and makes no allowance for differences between the expansions.

Much better agreement is obtained if we take a straight line characteristic on the  $H \log P$  diagram, which makes the heat-drop in each expansion proportional to the logarithm of the pressure-ratio. Taking the heat-drop as proportional to  $f''Z$  in Table II, the logarithm of the pressure-ratio for each expansion is obtained by multiplying the corresponding value of  $f''Z$  by the constant factor 0.922/19.42, in which the numerator is the logarithm of the ratio of the initial and final pressures, and the denominator is the sum of the values of  $f''Z$ . We thus obtain the values:

Table V.

Values of  $P$  by straight line characteristic on  $H \log P$  diagram.

Calculated from $f''Z$	129.1	100.4	77.4	59.1	46.3	35.3	26.6
Diff. (obs. - calc.)	- 1.4	+ 1.8	+ 0.3	- 1.4	- 0.1	+ 0.9	+ 1.1

The sum of the differences is now only + 1.2, showing that the assumed characteristic is a good first approximation. The straight line has previously been shown to correspond closely with an expansion curve of the type  $PV = kP^m$ , which will therefore be approximate for the available energy.

The simplest theoretical method of calculating the pressure-distribution in any case is from the expansion constant  $Z'$ . The pressure-drop  $DP$  for each expansion, if  $z_m$  and  $M$  are uniform, is obtained by multiplying the corresponding value of  $Z'$  by the constant factor  $145/17.08$ , in which the numerator is the difference of the initial and final pressures and the denominator the sum of the values of  $Z'$ . Adding the results in succession we easily find the following values of  $P$  at the intermediate points.

Table VI. Pressure-distribution assuming  $M$  and  $z_m$  uniform.

Calculated from $Z'$	130.5	102.3	79.6	61.1	47.9	36.4	27.2
Diff. (obs. - calc.)	-2.8	-0.1	-1.9	-3.4	-1.7	-0.2	+0.5

The differences considerably exceed the probable errors of observation, and show a systematic deviation, indicating that either  $M$ , or  $z_m$ , or both, were not the same for the different expansions, as assumed in the calculation.

In order to test whether  $z_m$  could possibly be the same for the different expansions, if  $M$  were constant, we must apply the method of § 159 in the last chapter, based on the discharge constant  $Z''$ , which is independent of  $z_m$ . Taking first the case of saturated steam, for which the turbine was probably designed, we find from equations (1), (2), and (3) of the last chapter the following mean values for the whole turbine over the pressure-range 164.7 (dry sat.) to 19.7 lbs.

$$\int uVdP = 90.8, \quad z_0 = 1.975, \quad m = 0.0923,$$

$$DH = 57.3, \quad V'' = 19.1, \quad D(P/V) = 58.1, \quad M = 123.0.$$

Taking the drop of  $P/V$  proportional to  $Z''$  for each expansion, we find:

Table VII.  $DP$ ,  $DH$ , and  $z_m$  calculated from  $Z''$  for saturated steam.

No	1	2	3	4	5	6	7	8	Sums
$DP$	34.14	28.32	22.44	18.52	13.12	11.53	9.23	7.70	145.0
$z_m$	1.965	1.975	1.948	1.970	1.960	1.968	1.977	2.015	1.973
$DH$	6.53	6.78	6.90	7.24	6.52	7.29	7.08	8.28	57.22
$P$	130.5	102.2	79.8	61.3	48.2	36.6	27.4		

It will be seen that the values of  $z_m$  are remarkably uniform, and that the values of  $P$  given in the last line, agree very closely, as they should, with those calculated from  $Z'$  in Table VI, but disagree with the observed values. The obvious inference is that

the steam in the trials was *not* saturated, with a uniform value of  $M$ , since that hypothesis makes  $z_m$  so nearly constant that the calculated values of  $P$  should have agreed closely with the observed.

If we repeat the calculation, as in Table VII, but for the case of dry supersaturated steam, we find that there is a systematic diminution of  $z_m$  as expansion proceeds, and the approximation to the pressure-distribution is about three times closer than in the case of saturated steam. But the irregular deviations persist, and it is unlikely that the steam would remain dry throughout the expansion, because the final state is below the SS limit, and we should expect some condensation to occur, even before the limit was reached, owing to the slow speed and the great extent of the blade surface.

The simplest way of obtaining an indication of the probable nature of the irregular deviations, is to take the ratio of the pressure-drop for each expansion calculated from  $Z'$  as in VI, to the observed pressure-drop, as in the following table, in which the variations of the ratio from unity include the effects of errors in  $P$  in addition to changes in  $M$  and  $z_m$ .

Table VIII. Ratio of pressure-drop (obs./calc.) in each expansion.

No.	1	2	3	4	5	6	7	8
<i>DP</i> obs.	37.0	25.5	24.5	20.0	11.5	10.0	8.5	8.0
„ calc.	34.2	28.2	22.7	18.5	13.2	11.5	9.2	7.5
Ratio	1.082	0.904	1.081	1.080	0.873	0.867	0.925	1.064

The irregularity of the ratios looks rather hopeless at first sight, but appears to be capable of a simple explanation. The high values in the first and last expansions are due simply to the neglect of receiver-drop. The sudden increase between (2) and (3) is due to an increase of  $M$ , consequent on by-passing steam to the end of the second expansion. The low values in (5) and (6) are caused by recovery from supersaturation, which sets in near the beginning of the fifth expansion. The rise in (7) and (8) shows that the steam is approaching more nearly the normal state of saturation. Owing to the change in  $M$ , and the uncertainty of the correction for receiver-drop, it is necessary to calculate the first four expansions separately in order to determine the value of the initial pressure, and the appropriate values of  $M$  for the first two expansions and



for the remainder of the turbine. The values thus obtained may be affected to some extent by errors in the pressure-differences, but appear to be substantially accurate.

### 165. Calculations for the Expansions in Succession.

In starting the calculation, it is necessary to make a preliminary estimate of the *initial pressure*, on account of the uncertainty of receiver-drop, otherwise we shall assume the observed pressures to be exact. The *initial state* of the steam may have been slightly superheated owing to throttling from boiler pressure, but we may take it as dry saturated without material error in the absence of more definite information. Estimating the receiver-drop as 8 per cent., we find

Initial state,

$$P' = 160 \text{ lbs.}, \quad \dot{V}' = 2.862, \quad H - B = 203.22, \quad aP'V' = 47.10.$$

Assuming the state to remain dry supersaturated through the first expansion, with the final pressure  $P'' = 127.7$ , as observed, we may calculate the final state as in XIV, § 150, but with the corrected values of the constants given in Table II.

$$(1) \quad \begin{aligned} DaPV &= 1.50, \quad \int aVdP = 10.45, \quad z_m = 1.929, \\ DH &= 6.33, \quad M = gf_1' DP/Z' z_m = 118.5. \end{aligned}$$

Similarly for the second expansion, with  $aP'V' = 45.60$ , we find

$$(2) \quad \begin{aligned} DaPV &= 1.50, \quad \int aVdP = 9.99, \quad z_m = 1.875, \\ DH &= 6.32, \quad M = 116.7. \end{aligned}$$

If we had assumed  $M = 116.7$  for the first expansion in place of assuming  $P' = 160.0$ , we should have found  $P' = 159.0$  for the initial pressure, which is within the limits of possible error. We conclude that the observed pressures are not inconsistent with the assumption that the mass-flow was the same in the first two expansions, and the state dry supersaturated.

Proceeding similarly for the third and fourth expansions, we find

$$(3) \quad \begin{aligned} DaPV &= 1.71, \quad \int aVdP = 11.85, \quad z_m = 2.023, \\ DH &= 7.26, \quad M = 129.3, \end{aligned}$$

$$(4) \quad \begin{aligned} DaPV &= 1.75, \quad \int aVdP = 12.35, \quad z_m = 2.046, \\ DH &= 7.62, \quad M = 127.9. \end{aligned}$$

It seems probable that there was an increase of at least 10.0 lbs. in  $M$  at the end of the second expansion. There was a leak-off from

the H.P. dummy at this point, and it would be natural, in making a record, to by-pass as much steam as possible to the end of the second expansion. To be strictly accurate, the initial value of  $H$  for the third expansion would require revision to allow for the addition of 10 lbs. of superheated steam, but this would add only 1 cal. to the initial value of  $H$ , and would not materially affect the results. Seeing that the value of  $M$  comes out the same for the third and fourth expansions within the probable limits of error of the pressure observations, it seems fair to conclude that there was a change in  $M$ , and that the condition of the steam remained dry and supersaturated at least to the end of the fourth expansion.

At the beginning of the fifth expansion, with  $H = 689.7$ , at  $P = 57.7$ , the steam, if dry, is already at a mean temperature nearly  $80^{\circ}$  C. below that of saturation. But the state will be far from uniform, so that parts may be much colder. There will probably be some condensation on the blades, even before this point is reached, because the current of supercooled steam will cool the blades below the saturation temperature.

Supposing that the steam remained dry throughout the fifth expansion, the pressure-drop required to get the same mass,  $M = 128$  lbs., through the expansion would be 14.6 lbs., which is 27 per cent. greater than the observed drop of 11.5 lbs. If on the other hand we supposed the steam instantaneously transformed into the saturated state at the beginning of the fifth expansion, and to remain in the equilibrium state of saturation without any retard in the condensation throughout the expansion, the pressure-drop required would be still greater, owing to the increased volume, and would amount to 15.7 lbs., which is 36 per cent. larger than that observed. It might appear at first sight as though the pressure-drop, if the steam were only *partially* transformed, should be somewhere intermediate between 14.6 for dry steam, and 15.7 for saturated steam, unless there were some mistake in the observations. But this is far from being the case, owing to the effect of the time-lag due to the finite rate of condensation (Callendar and Nicolson, *Proc. C. E.*, 1898). Owing to the time-lag, the greater part of the condensation will occur immediately *after* each step in the expansion, as the steam issues from the blades. The pressure-drop required to get the steam through each set of blades will be much the same as for supersaturated steam, and the increase of volume in passing through each blade-ring will also be the same. The condensation which occurs after passing the blades must produce a *rise* of

temperature, involving an increase of volume and velocity if the pressure remained constant. But since the velocity could not increase without increase of heat-drop and pressure-drop, we conclude that the volume will remain constant and the pressure will rise, making the back-pressure higher than the throat-pressure, which agrees with the result of the pressure-observations.

In order to account for the observed defect of pressure-drop in the fifth expansion, we have to suppose that only about 2 per cent. or 3 per cent. of the steam is transformed after each of the 28 steps in the expansion. Since the pressure is continually falling with production of fresh supersaturation at each step, it is evident that the effect will persist through two or three expansions, with a gradual reduction of intensity as the steam approaches more nearly the saturated state, since the rate of recovery will probably be proportional to the defect of temperature below the saturation point. A limit will be reached when the rate of recovery balances the rate of supersaturation. The final defect of temperature below the saturation point will probably be proportional to the rate of expansion.

It appears in the present instance, the rate of expansion being comparatively slow, that the final defect of volume would be only 1 or 2 per cent. below that of saturation, but the data do not permit a very exact estimate. Taking the final pressure as 20.7 lbs., allowing for receiver-drop, we could estimate the final volume as 18.84, and find a formula of the type  $PV = kP^m$  for calculating the available energy. This would give fairly accurate values for  $z$  and  $DH$  in each expansion, but, since the final state and pressure are uncertain, it is more instructive to calculate the last four expansions in succession, on the assumption that  $M$  remains constant, and that the state of the steam is *wet* supersaturated. The advantage of this procedure is that it becomes possible to determine the state of the steam at the end of each expansion, and affords a test of the consistency of the hypothesis above advanced of recovery from supersaturation.

In order to find the *least* increase of volume which will suffice to get the flow  $M = 128$  lbs./sec. through each of the expansions in succession, we employ the formula for the adiabatic heat-drop in the case of *wet* supersaturated steam, as given in Chapter IX, equation (85), namely,

$$[aVdP = (18/3) DaPV = (18/3) aP'V' (1 - (P''/P')^{2/13}) \dots (1)$$

In the case of the fifth expansion we have the initial state

$P' = 57.7$  lbs.,  $aP'V' = 40.61$ ,\* and take as a trial estimate of the drop  $DP$  the value  $DP = 14.6$  lbs. as above found for *dry* super-saturated steam. If  $M = 128$ , the trial value  $DP = 14.6$  requires a corresponding trial value of  $z$ , namely  $z' = 0.222DP/Z' = 2.095$ , by equation XIV (8). \*With  $P'' = 43.1$ , equation (1) gives

$$\int aVdP = 11.458,$$

whence  $z'' = (f_1' \int aVdP/Z)^{1/2} = 2.081$ . The difference,

$$z'' - z' = -0.014,$$

gives (by the rule in XV, § 158) the corrected value,  $z_c = 2.062$ , from which we obtain the corresponding corrected values of the pressure-drop,  $DP_c = 14.37$ , and of  $\int aVdP = 11.252$ . The value of  $DaPV$  is obtained from (1), giving  $aP''V'' = 38.01$ , and the final volume  $V'' = 8.528$ .

According to the theory above explained, the value of  $V''$  thus found will be that of the actual final volume in the fifth expansion, or the initial volume for the sixth, but the calculated value of the final pressure, namely  $P_c = 57.7 - 14.37 = 43.33$ , is lower than the observed pressure  $P_0 = 46.2$ , on account of the rise of pressure which occurs after each step in the expansion while the steam partially condenses with rise of temperature at constant volume. The effect of this is to reduce the pressure-drop in each step in the ratio  $DP_0/DP_c = 11.5/14.37$ , and to reduce the mean effective value of  $z$  in the square root of the same ratio, giving  $z_m = 1.844$ , as the value to be employed in calculating

$$DH = (2z_m - 1)f''Z = 6.00.$$

The tangent of the angle of discharge is reduced in the same ratio as  $z$ , owing to the reduction of the velocity; but the initial value of  $aPV$  for the next expansion is increased in the ratio  $P_0/P_c$ , giving  $aP_0V' = 40.52$  for the sixth expansion, nearly the same as the value 40.61 for the fifth.

Proceeding similarly for the three last expansions we find,

$$(6) \quad DP_c^* = 12.51, \quad z_c = 2.051, \quad V'' = 10.88, \\ DP_0^* = 10.0, \quad z_m = 1.834, \quad DH = 6.02.$$

$$(7) \quad DP_c = 9.74, \quad z_c = 2.004, \quad V'' = 13.85, \\ DP_0 = 8.5, \quad z_m = 1.872, \quad DH = 7.18.$$

$$(8) \quad DP_c = 8.08, \quad z_c = 2.080, \quad V'' = 18.06, \\ DP_0 = 7.0, \quad z_m = 1.890, \quad DH = 7.60.$$

The progress of the recovery towards saturation can be traced

by calculating the values of  $V_g$  for wet saturated steam at the same  $P$  and  $H$ , for comparison with the values of  $V''$  given above, as shown in the following table.

No.	1	2	3	4	5	6	7	8
$V''$ (SS)	3.472	4.105	5.303	6.843	8.528	10.88	13.85	18.06
$V_{g \text{ sat.}}$	3.515	4.303	5.523	7.232	8.840	11.03	14.07	18.33
Diff. %	1.2	2.5	4.0	5.4	3.5	1.4	1.7	1.5

The last line shows the percentage difference of volume from that of saturation, and illustrates the progress of supersaturation and recovery. The defect increases to a maximum at the end of the fourth expansion, where recovery sets in with a rapid diminution of the difference during the fifth and sixth. By the end of the sixth expansion the steam appears to have reached a steady state, remaining at a nearly constant percentage defect below saturation through the seventh and eighth, according to the method of calculation employed. The value of  $aPV$  remains practically constant from the end of the fourth to the end of the sixth expansion, while the most rapid recovery is in progress, but falls again in the seventh and eighth, when the rate of supersaturation balances the rate of recovery. Since the rate of expansion in this turbine was about the slowest on record, it is easy to see that when the expansion is twenty or thirty times more rapid, the beginning of condensation will be delayed to a lower pressure, and the defect of temperature and volume will remain much greater to the end of the expansion. Unfortunately there do not appear to be any equally satisfactory published data for the pressure-distribution in a high speed turbine.

There are many other points which could be investigated if the requisite observations were available, but special arrangements would be necessary for securing the appropriate data. The consistency of the calculated results in the present instance seems to show that the pressure-differences were fairly reliable, but the indicators employed, though doubtless the best of their kind, were not specially adapted for measuring small differences. Accurate pressure-observations at different loads and speeds, would probably suffice to clear up most of the remaining uncertainties.

When there is a change of state from dry to wet, the available energy cannot be obtained satisfactorily from a formula of the type  $PV = kP^m$ , with a single mean value of the index, but good

results may be obtained by using different values of  $m$  for dry and wet. In the present example, the value  $m = 0.1865$  for the first four expansions, and  $m = 0.0465$  for the last four, allowing for the change in  $M$ , give results for  $z$  and  $DH$  which are in very close agreement with those obtained by calculating the expansions separately.

**166. Effect of Condensation on the Blades.** In the foregoing calculation we have assumed for simplicity that  $M$  remains constant throughout the last five expansions, and that the whole of the observed defect of pressure-drop is to be explained by the recovery from supersaturation. But owing to the great extent of the blade-surface in the later expansions of a turbine of this type, the effect of condensation on the blades cannot be neglected as a contributory cause of loss. The condensation on the blades may be regarded as an indirect effect of supersaturation, since there would be no appreciable condensation on the blades unless they were cooled below the saturation temperature by the current of supercooled steam. According to the law of surface condensation (*loc. cit.*) the rate of condensation in lbs. per sec. per sq. ft., or other convenient units, will vary as the defect of temperature of the blades below saturation. There would be no great difficulty in measuring the actual temperature of the blades in any case, and in making a separate estimate of the condensation on the blades from the known value of the condensation constant. There are no data of this kind at present available, but it is easy to see that the defect of temperature of the blade-surface will be very small and approximately proportional to that of the steam below saturation, so that the rate of condensation on the blade-surface will vary in a similar manner to the rate of recovery of the steam from supersaturation, and will produce similar effects on the observed pressure-drop in each expansion. The values of the heat-drop as deduced from the observed pressure-drop, will be little, if at all, affected by any view with regard to the cause of the reduction of the pressure-drop, but in so far as it is attributed to blade-condensation, the power will be reduced in proportion to the reduction of  $M$ . Any water condensing on the blades will be quickly eliminated by centrifugal separation with a loss of kinetic energy  $u^2/2g$  per unit mass separated. There will be additional loss due to friction at the blade-tips, which may become serious if the turbine is not efficiently drained. But the chief loss of power will

be that due to reduction of  $M$  in all the subsequent expansions. Any drops of appreciable size occurring in the steam itself tend to be eliminated in a similar way, but the fine fog due to supersaturation may be treated as forming part of the mass of the fluid according to the usual assumption.

So far as the reduction of pressure-drop and heat-drop are concerned, it makes little or no difference, according to the foregoing theory, whether the condensation occurs on the blades or in the body of the steam, except that, if any condensation occurs on the blades, it involves a small reduction of  $M$  by centrifugal separation. Some condensation on the blades must undoubtedly occur, but the reduction of  $M$  by itself is far too small to account for the observed diminution of pressure-drop. At the end of the fourth expansion, where the defect of volume is a maximum, a total condensation amounting to only 3 per cent. of  $M$  would suffice to restore the steam to the state of saturation, but the reduction of pressure-drop, as compared with the pressure-drop required for saturated steam, is 86 per cent.

It might appear justifiable on this ground to ignore the reduction of  $M$  entirely as being relatively insignificant, but it appears that a small reduction of  $M$  is required in successive expansions to account satisfactorily for the observed effects. In the previous calculation, with  $M$  constant, it was assumed that the expansion of  $V$  was that due to adiabatic flow with the index  $3/13$ , in place of the usual index  $3f/13$ , in which the stage efficiency  $f$  takes account of the increase of volume due to friction in striking the blades. The pressure-drop thus found for wet supersaturated steam was 14.37 in expansion (5) with  $M = 128$ , as compared with 14.5 for dry supersaturated with the index  $3f/13$ . The final volume for wet supersaturated steam was taken as  $V'' = 8.528$ , on the tacit assumption that the rise of temperature due to friction was compensated, like that due to condensation, by the increase of back pressure after each step in the expansion. In reality the two effects of friction and condensation are not precisely similar. Condensation being merely a change of internal state without addition of external energy, cannot involve any increase of intrinsic energy  $E$ ; but the conversion of kinetic energy into heat by friction necessarily requires an increase of  $E$ , which should be taken into account in the usual way. This would make little difference in one expansion but, the effect being cumulative, we should soon arrive at excessive values of  $V$ , if allowance were not made for the reduction of  $M$ .

by blade-condensation, which appears to be of the right order of magnitude to compensate for the effect of friction in increasing  $V$ .

**167. Data for the L.P. Turbine of SS. *Mauretania*.** The following are the material dimensions of the L.P. turbine. Diameter of rotor, 140 inches, with eight expansions, the first four of 7 stages each, the last four of 8 stages each. The first five expansions with normal blades, the last three with "semi-wing," "wing" and "double-wing" blades, respectively. The ratios actually employed in gauging the apertures of the wing-blades do not appear to have been published. We shall therefore assume  $\alpha = 70^\circ$ ,  $\tan \alpha = 2.748$  for the normal blades, as in the H.P. turbine, and shall take the values of  $\tan \alpha$  for the last three expansions as being 1.832, 1.222, and 0.814 respectively, diminishing in the simple ratio  $2/3$  for each expansion.

The variation of blade-angle involves a small corresponding variation in the efficiency constant  $f_1'$ , as explained in Chapter XIV, § 149. The exact nature of this variation remains at present uncertain, but it appears that we cannot be far wrong in assuming the simple formula

$$f_1' = 1 - 0.117/\sin^2(\alpha + 20^\circ), \dots\dots\dots(2)$$

which makes  $f_1'$  a maximum and equal to 0.883 when  $\alpha = 70^\circ$ , as previously assumed; and makes  $f_1'$  vanish, as it should, when  $\alpha = 0^\circ$ . The resulting diminution of  $f_1'$  is only 5 per cent. for the double-wing blades. The formula takes no account of the radial divergence of the blades, which probably involves some additional loss in the case of long blades of uniform section.

Table IX.

Dimensions and constants for L.P. turbine at 494 revs./min.

No.	1	2	3	4	5	6	7	8	Sums
$N$	7	7	7	7	8	8	8	8	60
$x$ in.	81	104	138	17	22	22	22	22	—
$X$ in.	3842	4964	6444	8385	11200	11200	11200	11200	—
$\tan \alpha$	2.748	2.748	2.748	2.748	2.748	1.832	1.222	0.814	—
$f_1'$	0.883	0.883	0.883	0.883	0.883	0.879	0.868	0.841	—
$Z$ calcs.	2.446	2.522	2.620	2.744	3.338	3.338	3.338	3.338	23.664
$f''Z$ calcs.	2.316	2.416	2.536	2.672	3.271	3.291	3.304	3.311	23.117
$Z'' \times 10^4$	6061	4798	3789	2995	2656	1783	1193	796	24071
$Z'' \times 10^7$	4798	2916	1751	1044	675.1	304.3	136.2	60.64	11686
$DP$ , lbs.	4.716	3.733	2.950	2.339	2.066	1.387	0.928	0.619	18.73
$DP$ , lbs.	4.971	1.965	3.314	2.822	2.455	1.228	0.982	0.982	18.75



The values of the coefficient  $f''$  are calculated by the formula,  $f'' = (x - l)/(x + 2l)$ , with the tip-clearance  $l = 0.15''$ , proportional to that assumed for the H.P. turbine, but, owing to the length of the blades, the correction makes little difference to the results. In the case of the wing-blades, the factor 2 is replaced by the proper value of  $\sec \alpha - 1$ . The values of  $Z'$  and  $Z''$  are calculated with the appropriate leakage corrections and values of  $\tan \alpha$ .

The last line in the table shows the pressure-drop  $DP_0$  observed in each expansion, taking the initial pressure as 5 lbs. (gauge), and the final pressure as 28 inches vacuum (bar. 30 ins.), or 19.73 lbs. and 0.982 lb. absolute. The last line but one, headed  $DP_z$ , shows the pressure-drop for each expansion calculated from  $Z'$  on the assumption that  $M$  and  $z$  are the same for each expansion, and that the initial and final pressures are 19.73 lbs. and 1 lb. abs., respectively. The differences suggest, as in the case of the H.P. turbine, (1) that corrections are required for receiver-drop, (2) that there is a considerable change in  $M$  at the end of the second expansion, (3) that there is a change in state of the steam at the end of the fifth.

Assuming that the turbine was designed for saturated steam with a pressure-range from 5 lbs. (gauge) to 28 in. vac., it is first necessary to see whether the dimensions assumed will give a uniform value of  $z$  under these conditions if  $M$  is the same for each expansion. From equations XV (1) and (2), neglecting the variation of  $f_1'$ , we find for the whole turbine the approximate mean values,  $DH = 69$ ,  $V'' = 316$ ,  $m = 0.0855$ ,  $D(P/V) = 0.967$ . From which, by equation XV (12), we deduce  $M = 110.4$ . This value of  $M$  is so much smaller than the value  $M = 123$  similarly obtained for the H.P. turbine, that it would evidently be impossible to get the still larger flow  $M = 128$  through the L.P. turbine unless a considerable proportion of the steam were by-passed to the end of the second expansion. It would appear that the L.P. turbine of the *Mauretania* was not designed (as in the case of the *Dreadnought*) to utilise the auxiliary exhaust, which is stated to have been employed for heating the feed-water. The uniformity of the values of  $z$  calculated from  $Z''$  by the method of XV, § 159, as shown in the following Table X, indicates that the dimensions assumed are in all probability substantially correct, confirming the ratio 2/3 selected for successive values of  $\tan \alpha$  in the last four expansions.

Table X.

L.P. turbine.  $DP$ ,  $z_m$ , and  $DH$ , calculated from  $Z''$ .  $M = 110.4$ .

No.	1	2	3	4	5	6	7	8	Sums.
$DP$	4.747	3.721	2.918	2.311	2.087	1.392	0.932	0.640	18.75
$z_m$	1.999	1.980	1.966	1.970	2.006	1.993	1.995	2.052	—
$DH$	6.94	7.15	7.43	7.86	9.85	9.83	9.77	9.74	68.57

Assuming the steam to remain saturated throughout, if the object is to keep  $z_m$  uniform, it appears that the choice of dimensions could scarcely have been improved. The change of  $z_m$  from 1.970 in (4) to 2.006 in (5) indicates that a slightly larger increase of  $x$  than from 17" to 22" would have been required to compensate for the change from 7 to 8 stages, and to make the *mean* value of  $z$  the same in the fourth and fifth expansions. On the other hand, a smaller change of  $x$  would have sufficed to make the *initial* steam-velocity the same, a condition which appears to be frequently adopted in design. The high value of  $z$  in the last expansion would be corrected by a slight change in the final pressure, as from 28" vac. to 1 lb. abs.; and would be over-corrected by making allowance for the probable variation of  $f_1'$  as shown in Table IX. We infer from the want of correspondence between the observed and calculated results for  $DP$ , that the steam did *not* remain saturated, and that  $M$  was *not* the same for all the expansions. The values of  $DH$  given in the table include the effect of the assumed variation of  $f_1'$ .

### 168. Calculation for the Expansions in Succession.

As in the case of the H.P. turbine, we may proceed to calculate the flow for each expansion in succession on the assumption that the observed pressures are exact. They have generally been regarded as impossible to interpret, and are doubtless more uncertain than those for the H.P. turbine. They appear, however, to be sufficiently correct to afford a good illustration of the method of calculation, and a fairly clear indication of the state of the steam.

Before making the calculation, we require an approximate estimate of the state and probable behaviour of the steam. According to the previous calculation, the steam leaving the H.P. turbine will be but slightly supersaturated. The superheated steam arriving from the H.P. dummy will clear up the fine fog, leaving a mixture of saturated steam with comparatively few drops of

water in suspension. Most of these will be separated out by the moving blades, and the mixture can be treated as dry supersaturated for the first part of the expansion, since no fresh nuclei will be generated until the temperature has again fallen to the supersaturation limit.

It is well known that vacuum gauges are apt to be somewhat vague in their indications in the neighbourhood of atmospheric pressure, but if we take the pressure to be exactly atmospheric, 30" of mercury, or 14.73 lbs. abs. as observed at the end of the first expansion, with a drop of 4", or 1.964 lbs., in the second expansion, it is possible to calculate the initial pressure, as in the case of the H.P. turbine, on the assumption that  $M$  is the same for the first two expansions and the state dry supersaturated. Taking  $m = 0.146$  as a probable value of the index, we find the drop of  $P^{2-m}$  for the second expansion to be 34.14, which when increased in the ratio  $Z_1''/Z_2''$  gives 56.16 for the drop of  $P^{2-m}$  in the first expansion; whence the initial value of  $P$  is 17.546 lbs., with  $DP = 2.816$ . Having found the pressures, the exact value of  $H$  makes comparatively little difference to  $M$  or  $z$ . Estimating the initial value of  $H$  as 639, with a drop  $DH = 9$  for the first two expansions, we find  $M = 82.7$  from XV (12), giving (1)  $z = 1.60$ ,  $DH = 5.1$ , (2)  $z = 1.40$ ,  $DH = 4.34$ , for the two expansions separately.

If we suppose that the usual excess of H.P. dummy leakage over L.P. dummy leakage is sufficient to make up for the loss of water by separation and drainage, we should expect to find the flow through the remaining expansions of the L.P. turbine nearly the same as the value  $M = 128$  found for the latter part of the H.P. turbine. The value  $M = 83$  for the first two expansions of the L.P. turbine implies that about a third of the total steam was by-passed to the end of the second expansion. This would explain why the observed pressure-drop in the second expansion is only half the normal, and the absolute pressure at the end of the second expansion is 13 per cent. above the normal for the pressure-range, and also why the receiver-drop is twice as great as that found at the end of the H.P. turbine. Assuming on these grounds that about one-third of the steam was by-passed at constant  $H$ , retaining the initial value  $H = 639$ , with two-thirds at  $H = 630$  after passing through the two expansions we find  $H = 638$  as a probable estimate of the initial state of the steam at the beginning of the third expansion.

Taking the observed pressures as correct for the next three expansions and assuming the state dry supersaturated, we find:—

Table XI. L.P. Turbine. Results for expansions (3), (4), and (5).

Initial state (3),	$P' = 12.766$ ,	$H' = 633$ ,	$V' = 29.73$ ,	$aP'V' = 39.03$ ,
• Final state (3),	$P'' = 9.451$ ,	$z_m = 1.966$ ,	$P'H = 7.44$ ,	$M = 126.5$ .
„ (4),	$P'' = 6.629$ ,	$z_m = 2.036$ ,	$DH = 8.21$ ,	$M = 131.6$ .
„ (5),	$P'' = 4.174$ ,	$z_m = 2.046$ ,	$DH = 10.11$ ,	$M = 128.4$ .

The values of  $M$  found agree as closely as can be expected, considering that the pressure readings were taken only to the nearest  $1/4''$ , and that the calculated value of  $M$  depends on the small pressure-difference. The mean of the three values, namely  $M = 128.8$ , will give a better approximation to the actual flow. The mean value of  $M$  similarly found for the third and fourth expansions of the H.P. turbine was  $M = 128.6$ . The agreement may be taken as a fair corroboration of the method of calculation adopted.

If we take  $M = 128$ , and calculate the pressure-drop for the next expansion on the assumption that the steam remains dry and supersaturated, the result found is greatly in excess of the observed value. The observed defect might naturally be attributed to some want of efficiency of the wing-blades, or to some uncertainty in the angles assumed, if it were not that the values of  $z$  for the wing-blades agree so closely with each other in Table X, and that a similar defect of pressure-drop occurs in the H.P. turbine, where there is no reason to suspect any variation in the blade-angles. The effect may reasonably be attributed, as in the previous instance, to the time-lag in condensation, which produces a rise of back-pressure at each step of the expansion, while the steam is recovering rapidly from the state of supersaturation. The results for the last three expansions might be calculated by the same method as for the H.P. turbine, but since the pressure-differences become very small towards the end, and the exact method employed in gauging the blades is uncertain, it will suffice for practical purposes if we take  $PV$  as constant through the sixth and seventh expansions (as found in the case of the H.P. turbine during recovery) with  $aPV = 33.0$ , the value at the end of the fifth expansion. We thus obtain the following results for the last three expansions, in which the final pressure is estimated at 1.22 lbs. abs.

The mean effective value of  $z$  in each expansion is determined chiefly by the observed pressure-drop, and the value of  $DH$  is little affected by any assumptions which may be made with regard

Table XII. L.P. turbine. Results for expansions (6), (7), and (8).

Initial state (6),  $P' = 4.174$ ,  $H' = 607.24$ ,  $V' = 77.0$ ,  $\alpha P' V' = 33.00$ .

Final state (6),  $P'' = 2.946$ ,  $z_m = 1.741$ ,  $DH = 8.17$ ,  $V'' = 109.0$ ,  $Z' = 1549$ .

" (7),  $P'' = 1.964$ ,  $z_m = 1.866$ ,  $DH = 9.02$ ,  $V'' = 163.5$ ,  $Z' = 1142$ .

" (8),  $P'' = 1.220$ ,  $z_m = 1.980$ ,  $DH = 9.81$ ,  $V'' = 255.0$ ,  $Z' = 789$ .

to the rate of recovery. The simple assumption  $PV = \text{constant}$  gives a probable rate of recovery in the sixth and seventh expansions. In the last expansion it is assumed that the steam has reached a steady state, which serves to fix the final pressure with a fair degree of certainty. The leaving-loss, with the revised value of the final pressure as here given, comes out approximately 1.7 cal. C., in place of the value 1.5 cal. as previously estimated in Chapter XI, § 121. The value of  $DH$  in the last expansion, as calculated from  $z$ , is automatically corrected for leaving-loss.

The reduction of  $z$  by recovery from supersaturation involves a proportional reduction in  $Z'$  and  $\tan \alpha$ , which are not required in the calculation of  $DH$ , but are readily found from  $z$  by the relation  $Z' = g f_1' DP / M z_m$ , XIV (3), with the known value of  $M$ , namely 128.8 in the present case, if we neglect loss by separation and drainage. The values of  $Z'$  thus found afford a check on the calculation, especially in respect of the final value of  $P$ , since  $Z'$  for (8) cannot be greater than the value  $796 \times 10^{-4}$  given in Table IX for normal flow. Thus the final pressure in the present instance cannot be less than 1.210 which would make  $Z'$  equal to the tabulated value, but may be 1 or 2 per cent. higher than 1.22, if we admit the reduction of  $M$  by a similar amount. These differences are beyond the limits of accuracy of the actual pressure measurements, which are accepted as correct for the sake of indicating the kind of information which could be obtained from more accurate observations.

The progress of supersaturation and recovery can be traced, as in the case of the H.P. turbine, by comparing the values of the final volume  $V''$  in each expansion with those calculated for saturated steam at the same  $P$  and  $H$ .

Table XIII. L.P. turbine. Supersaturation and Recovery.

No.	1	2	3	4	5	6	7	8
$V''$ (SS)	25.89	29.11	38.36	51.91	77.00	109.0	163.5	255.0
$V_{\text{sat}}$	26.45	30.10	39.83	55.10	84.10	115.8	167.7	260.2
Diff. %	2.1	3.0	3.7	5.2	8.5	5.8	2.5	2.0
$1 - q$ %	1.0	1.5	1.6	2.4	3.4	4.1	5.0	6.0

The first line gives the number of the expansion, the second the actual final volume of the supersaturated steam at the end of each expansion.  $V_g$  shows the corresponding volume for saturated steam at the same  $P$  and  $H$ . The next line shows the defect of volume due to supersaturation, expressed as a percentage of  $V_g$ . The last line shows the percentage wetness of  $V_g$ , or the defect of volume of the equivalent wet saturated steam from dry saturated at the same pressure and temperature.

**169. Revision of the SS Limit.** Comparing these results with the similar table given for the H.P. turbine, we observe that condensation is delayed to a later stage in the L.P. turbine, and that the defect of volume when condensation begins is considerably greater than in the H.P. turbine. On the other hand, the time interval from the first row of blades to the end of the fourth expansion in the H.P. turbine is nearly double that taken by the steam in passing from the beginning of the first to the end of the fifth expansion in the L.P. turbine. The fact that the expansion is twice as rapid is hardly sufficient by itself to account for the increase of supersaturation. According to the estimate above made of the state of the steam in the L.P. turbine, the point at which condensation starts is within one or two calories of the SS limit, as defined on the basis of Wilson's experiments with moist air at  $20^\circ \text{C}$ ., which we should expect to be fairly reliable at low pressures, though possibly erroneous at high pressures. The point at which condensation starts in the H.P. turbine is considerably above the SS limit given by Wilson's experiments, but the pressure is 14 times higher than in the L.P. turbine. The chief point in common is that the equivalent wetness  $1 - q$  is nearly the same in the two cases, namely 3.1 per cent. for the H.P. turbine and 3.4 per cent. for the L.P. This relation, if true, would give a simple definition of the limit, which would be applicable even at the critical point, in the neighbourhood of which the phenomenon of cloudy condensation is still well-marked.

There is so little direct experimental evidence with regard to the point at which condensation begins in a turbine or nozzle at high pressures, that we cannot afford to neglect so clear an indication as that afforded by the analysis of the pressure-distribution in the *Mauretania*. In point of fact, a large slow-speed turbine is remarkably well suited to indicate the beginning of condensation, because the initial rate of recovery is high compared with the

rate of expansion, so that the point in question is sharply marked. With a higher rate of expansion, the change would be more gradual, and it would be more difficult to locate the commencement. The gradual transition would simulate delay, and lead to an overestimate of the true limit. Allowing for the difference of steam-speed in the H.P. and L.P. turbines, we shall probably not be far wrong if we take the SS limit, as indicated by these observations, to occur at an equivalent wetness of 3 per cent., which agrees very closely with the Wilson limit at lower pressures. The limit thus defined has the advantage that it is much simpler in application than the Wilson limit, because it does not require a special table. The value of  $H_{ss} = H_s - 0.03(H_s - st)$ , is readily deduced from the values of  $H$  and  $t$  at the observed pressure by reference to the ordinary tables for saturated steam. The value of  $V_{ss}$  for dry steam at the SS limit is most easily deduced from that of  $V_s$  for dry saturated steam at the same pressure by subtracting  $0.03(H_s - st)/p$ , which is easily worked on a small slide-rule. The actual value of  $V$  for the wet mixture in rapid expansion at the SS limit may be obtained by the usual formula for wet saturated steam, but with  $H_{ss}$  and  $V_{ss}$  in place of  $H_s$  and  $V_s$ .

The Wilson limit, if applied at high pressures, is liable to the theoretical objections, (1) that it makes the defect of temperature below the saturation value more than twice as great at 100 lbs. as at 1 lb., whereas it should be less than at 1 lb., and (2) that it gives results which are obviously impossible in the neighbourhood of the critical point. The limit as above defined by 3 per cent. of equivalent wetness, escapes both these objections. The adoption of the latter limit, in place of Wilson's, makes no difference to the discharge through a nozzle, and scarcely affects any of the calculations extending to low pressures, but necessarily makes a material difference in estimating the point at which condensation starts, and the nature of the flow at high pressures.

In proposing the revision of a limit which has been accepted for so many years, it is desirable to give some confirmation of the correctness of the calculations on which the revision is based, which might otherwise appear purely speculative. The most direct verification obtainable from the data given in the trials of the *Mauretania* is by calculating the total horse-power. This is easily done by adding the values of  $M \times DH/0.8928$  for the separate expansions as above calculated, which gives 17,570 horse-power for the H.P. turbine, and 19,290 horse-power for the L.P., a total

of 86,860 horse-power. The actual total does not appear to have been published for the high-speed trials at 194 revs./min., but can be deduced from the observed value 34,000 for each complete turbine at a mean speed of 190 revs. in the 24 hours trial. Assuming that the total power for a marine turbine of this type varies as the cube of the mean speed, which may be closely verified over a wide range from the trials of H.M.S. *Dreadnought*, the power at 194 revs. would be 36,200. Allowing for small losses which are not included in the calculation for the separate expansions, the results agree as closely as could be expected.

It would appear from these illustrations of the effects of supersaturation that the actual expansion of the steam never follows the usual saturation state as a limit even in the case of a slow-speed turbine. It must not however be inferred that all calculations based on the assumption of the saturated state are necessarily erroneous and useless. Thus if the SS limit as defined by reference to the value of  $H$ , corresponds to 3 per cent. of equivalent wetness, the ordinary saturation tables will afford in most cases a fair first approximation to the performance, and the effect of small variations of speed or pressure can be worked out on this basis without material error as previously illustrated. On the other hand, there are many cases in which the effects of supersaturation make an essential difference, as in working out the pressure distribution, or the effect of superheat for a particular machine. We have endeavoured to show that the experimental results in such cases cannot be explained satisfactorily without making allowance for the effects of supersaturation as deduced from the known physical properties of steam. Without fresh experimental evidence, specially designed to elucidate the points which remain uncertain, little would be gained at the present stage by multiplying examples based on imperfect observations. Enough has been said to make out a *prima facie* case for new methods of calculation and experiment, and to indicate the desirability of cooperation between the engineer and the physicist in the adaptation of the heat-engine to suit the properties of the working fluid. "



## APPENDIX I

### THERMODYNAMICAL RELATIONS

**179. Expression in terms of Partial Differential Coefficients.** Many of the most familiar and important quantities with which we have to deal, such as the specific heats, and the pressure and expansion coefficients, are most conveniently and accurately expressed in the notation of partial differential coefficients, which has the great advantage of indicating at a glance the exact nature of the quantity denoted, and the experimental conditions under which it is measured. The majority of students seem to regard a partial differential coefficient as a mystic symbol, unintelligible without a long and arduous training in the intricacies of the calculus. This feeling is apt to be fostered by a purely symbolical treatment of the subject, but tends to disappear if it is approached from an experimental standpoint. For the present purpose the experimental application is the most important, and purely mathematical aspects of the method may be ignored. It is possible to attain a very fair idea of the meaning and use of the notation for experimental purposes without an elaborate mathematical training. Many of the relations most often required in practice receive little attention in theoretical works, while on the other hand many formal points are elaborated which are of little importance in the practical application. It has therefore been decided to include in the present work a brief explanation of the notation, with illustrations of its practical application, in the hope that it may help the student to a better understanding of the experimental requirements, which are naturally to a great extent overlooked in purely mathematical treatises. Some students on the other hand are quite happy so long as they are dealing with pure symbols, but have a natural distaste for applying them to numerical calculations. For such a little exercise in physical arithmetic is highly beneficial. To avoid bewildering the student with all the possible permutations and combinations of the various symbols, the illustrations will be drawn almost exclusively from those relations which have a direct bearing on the subject of the

present work. Many other relations of a similar character will be found in mathematical works, but though important as illustrating the symmetry of the formal relations between the various quantities, they are not independent results, and merely amount for the most part to saying the same thing in a great many different ways, which is unnecessary for practical purposes.

**171. The Expansion Coefficient.** One of the most familiar types of a differential coefficient is the coefficient of expansion. This coefficient is measured in practice by observing the change of volume  $v' - v''$  produced by a change of temperature  $t' - t''$  and taking the ratio  $(v' - v'')/(t' - t'')$ . Since  $v$  represents the volume of unit mass, the coefficient thus found expresses the mean rate of expansion of unit mass per  $1^\circ$  rise of temperature over the range of the experiment. The mean coefficient over any range will in general be nearly the same as the actual rate of expansion per  $1^\circ$  at the middle point of the range, provided that the range is small.

The actual value of the coefficient *at a point*, as opposed to the mean value over a range, is denoted by  $dv/dt$ , and is defined as the limiting value of the ratio of the difference in volume  $dv$  to the difference in temperature  $dt$ , when the differences are infinitesimal. The value of  $dv/dt$  cannot actually be determined in this way, but it may be inferred with considerable precision from observations over an extended range, either by graphic methods, or preferably by finding a formula to represent the observed values of the volume in terms of the temperature, and deducing the corresponding expression for  $dv/dt$  at any point by differentiation. It will be assumed that the student is familiar with the rules for differentiating simple functions.

In the case of a liquid it is seldom necessary to specify the pressure under which the volume is observed, because the change of volume with change of pressure is usually small. But in the case of a gas or vapour, the effect of pressure on the volume is generally of the same order as the effect of temperature, and the coefficient of expansion is usually measured under the condition of constant pressure. This is commonly denoted by adding the suffix  $p$ , thus  $(dv/dt)_p$ , which implies that the pressure is to be kept constant during the measurement, or treated as constant in the differentiation. Thus for an ideal gas obeying the law  $V = RT/aP$ , the value of the coefficient  $(dV/dT)_p$  is simply  $R/aP$ , and is constant if  $P$  is

constant, but has different values at different pressures, when measured per unit mass.

The coefficient of expansion of a gas at constant pressure is most often tabulated in terms of the volume at  $0^{\circ}\text{C}$ . under the same pressure, and not in terms of unit mass. These tabulated values correspond with the formula  $(dV/dT)_P/V_0$ , and are obtained by dividing the observed values of the coefficient per unit mass by  $V_0$ , the volume of unit mass at  $0^{\circ}\text{C}$ . under the same pressure. In the case of an ideal gas the coefficient thus measured is constant and equal to  $1/T_0$ , where  $T_0$  is the absolute temperature corresponding to  $0^{\circ}\text{C}$ . But the coefficient most often required in the equations of thermodynamics is simply  $(dV/dT)_P$ , measured per unit mass.

In the case of actual gases and vapours the coefficient of expansion varies with temperature as well as with pressure, and often deviates considerably from the ideal value. The case of steam may be taken as typical. According to the author's equation the volume is given by the expression,  $V = RT/aP - c + b$ , where  $b$  is constant, and  $c$  varies as  $T^{-n}$ . The corresponding expression for  $(dV/dT)_P$  is  $R/aP + nc/T$ , the value of which at any temperature and pressure is easily found from the table giving values of  $c$ . The numerical value of the coefficient may also be obtained from Table V as follows:

*Example 1.* Find from Table V the values of the coefficient  $(dV/dT)_P$  at 100 lbs. pressure and at temperatures  $195^{\circ}$ ,  $200^{\circ}$ , and  $205^{\circ}\text{C}$ .

The value of  $(dV/dT)_P$  at 100 lbs. and  $195^{\circ}\text{C}$ . is found by taking the difference, 0.1211, between the tabulated values of  $V$  at  $190^{\circ}$  and  $200^{\circ}\text{C}$ ., and dividing by 10, which gives 0.01211. Similarly at  $205^{\circ}\text{C}$ . we find 0.01200. At  $200^{\circ}$  divide the difference between  $V$  at  $190^{\circ}$  and  $V$  at  $210^{\circ}$  by 20, which gives 0.012055. The coefficient is nearly constant, and the values thus found are correct to 1 in 2000 at the mean points, although the differences are far from being infinitesimal. If steam behaved as an ideal gas the value at 100 lbs. would be  $R/aP$  or 0.010706. The actual value at  $200^{\circ}\text{C}$ . by the formula  $R/aP + nc/T$  is 0.012051, taking  $n = 10/8$ , and  $c = 0.1909$  at  $200^{\circ}$ .

*Formula for Small Differences.* When the coefficient  $(dV/dT)_P$  is known at any particular temperature and pressure, the change of volume  $V' - V''$  for any small change of temperature  $T' - T''$

at constant pressure may be found with considerable accuracy from the formula  $(dV/dT)_P(T' - T'')$ , which may be written  $(dV/dT)_P dT$ , and is mathematically exact in the limit when the change  $dT$  is infinitesimal. The result would be exact for any change of temperature, however great, if the coefficient were constant. In general the coefficient is so nearly constant that the relation may be applied in practice without material error for a range of  $5^\circ$  or  $10^\circ$ . Thus to find  $V$  at  $20.5^\circ$  and 100 lbs., we have only to add  $5 \times 0.01200$  to  $V = 4.8901$  at  $20^\circ$ ; giving the result  $V = 4.9501$ , correct to the last figure with very little trouble.

*Interpolation.* The above example illustrates the method of interpolation by simple proportion, which corresponds exactly with the formula for small differences, since it rests on the same fundamental assumption, namely that the change of  $V$  is *proportional* to the change in  $t$  when the difference is small. The smaller the difference, the greater the accuracy of this assumption, but for experimental purposes there is no advantage in reducing the differences between the tabulated values below the point which permits an accuracy of interpolation equivalent to the last figure tabulated. With the aid of a small slide-rule, it is much less trouble to obtain intermediate values at any required point from a table by interpolation than to calculate them with equal accuracy from a formula. There is also less liability to serious error since the differences involved are relatively small.

The differential coefficient  $(dv/dt)_P$  may be regarded as the coefficient of proportionality by which the difference in  $t$  must be multiplied in order to find the corresponding difference in  $v$ , when the pressure is constant. It is called a *partial* differential coefficient because it gives only that part of the change of volume which is due to change of temperature.

The formula for the change due to temperature remains equally valid if the pressure changes in addition to the temperature, but in order to find the *total* change of volume due to the combined effects of temperature and pressure, it is necessary to add the separate effects, which each would produce if the other remained constant. Provided that the changes considered are small, the two effects may be treated, both mathematically and experimentally, as though they were independent of each other.

**172. The Compressibility.** The effect of pressure in changing the volume may similarly be expressed in terms of a

coefficient, called the compressibility, which is measured by observing the change of volume  $dv$  produced by a change of pressure  $dp$ , and taking the limiting value of the ratio  $dv/dp$ . If the compressibility is required free from any effect due to change of temperature, it is necessary to perform the experiment under the condition of constant temperature. The compressibility so measured is called the "isothermal" compressibility, and is denoted by  $-(dv/dp)_t$ , per unit mass, where the suffix  $t$  indicates that the temperature is supposed to remain constant during the measurement. The algebraic sign of the compressibility is taken as negative, because an increase of pressure invariably produces a diminution of volume. It is easy in practice to determine the isothermal compressibility by allowing time for the temperature to regain its original value when the rise produced by compression has disappeared. But it is also possible, by taking instantaneous readings and in other ways, to determine the value of the "adiabatic" compressibility, denoted by  $-(dv/dp)_Q$  under the condition that  $Q$  is constant, or that no heat is allowed to escape. The value so found is materially different from the isothermal compressibility, because the rise of temperature tends to reduce the diminution of volume.

- When the isothermal coefficient  $(dv/dp)_t$  is known, the change of volume  $dv$  due to any small change of pressure  $dp$  at constant temperature is given by the expression  $(dv/dp)_t dp$ , which is exact in the limit when the change is infinitesimal. The value of this coefficient for steam, obtained by differentiating the expression for  $V$  with respect to  $P$  at constant  $T$ , is  $-RT/aP^2$ , the same in form as for a perfect gas obeying Boyle's law.

*Example 2.* Find from the tables the value of  $(dV/dP)_T$  for steam at  $200^\circ\text{C}$ . and 95 lbs. Compare the result with the formula  $-RT/aP^2$ , and deduce the value of  $V$ , where  $T^* = 473.1^\circ$ ,  $R/a = 1.0706$  (F.P.C.).

The difference between the tabular values of  $V$  at 90 and 100 lbs. is found to be  $-.5628$ , which gives  $-.05628$  for the mean coefficient per lb. over this range. The formula gives  $^o$

$$-1.0706 \times 473.1/95^2,$$

or  $-.05612$  for the coefficient at 95 lbs., which differs by nearly 8 in 1000 from  $0.05628$ , because the mean coefficient is not exactly equal to the coefficient at the mean point, when the pressure difference is 10 per cent., as in this example. The volume at 95,

found by adding  $-0.5628 \times 5$ , or  $-2.814$ , to the volume at 90, is 5.1715, which is similarly inexact.

The compressibility, like the coefficient of expansion, is most often tabulated in terms of unit volume in place of unit mass. The value per unit volume is obtained by dividing  $-(dV/dP)_T$  by  $V$ , the volume of unit mass. The reciprocal of the compressibility per unit volume is called the "elasticity," and is given by the expression  $-V(dP/dV)_T$ , being taken with the negative sign, like the compressibility, because the numerical value of  $dP/dV$  is always negative. The adiabatic elasticity is defined by the same expression as the isothermal elasticity, except that the ratio  $(dP/dV)_Q$  is to be taken under the condition that no heat is allowed to escape. It is always greater than the isothermal elasticity, except at a point of maximum density, when the two elasticities become equal, as in the case of water at  $4^\circ \text{C}$ . In the case of a substance obeying Boyle's law,  $PV = K$ , we have the simple relation

$$-V(dP/dV)_T = +P,$$

at constant temperature. In the case of steam, the isothermal elasticity takes the form  $P(dPV/RT)$ , which is a little less than  $P$  on account of the deviation from Boyle's law.

The value of a partial differential coefficient, such as  $(dV/dP)_Q$ , depends essentially on the condition under which the ratio is taken, as in the case of  $(dV/dP)_T$  and  $(dV/dP)_Q$ , which are different for a given substance at the same temperature and pressure, but are related in a symmetrical manner, as explained in § 175.

When two different coefficients of the same quantity, such as  $(dV/dP)_Q$  and  $(dV/dT)_Q$ , are taken under the same condition, the usual relation

$$(dP/dT)_Q = (dV/dT)_Q / (dV/dP)_Q = (dP/dV)_Q (dV/dT)_Q$$

applies to the ratio, since the change of  $V$  is taken under the same condition of adiabatic compression in both cases, and can be eliminated. But this relation no longer applies when the change of  $V$  is taken under different conditions, as in  $(dV/dP)_T$  and  $(dV/dT)_P$ , the ratio of which is *not*, either  $(dP/dT)_P$  (which is zero), or  $(dP/dT)_T$  (which is infinite), but has the value  $-(dP/dT)_P$ , as shown in § 174.

**173. Formula for the Mean Coefficient of Compressibility.** The accurate interpolation of  $V$  has always been a difficulty owing to the rapid variation of the coefficient of compressibility

with pressure, namely as  $1/P^2$ , for a substance obeying Boyle's law. For this reason values of the volume are often tabulated for each single pound of pressure. But this is not really necessary in the case of superheated steam, because the formula for the mean coefficient of compressibility between finite limits is very simple, and exact values at intermediate points are readily obtained when required even for large pressure differences.

If  $V'$ ,  $V''$  are any two values of the volume at different pressures  $P'$  and  $P''$ , but at the same temperature  $T$ , it follows from the characteristic equation that the difference of the volumes  $V' - V''$  is equal to  $RT/aP' - RT/aP''$ . Dividing the difference of the volumes by the difference of the pressures, we accordingly obtain the following simple and exact expression for the mean coefficient between  $P'$  and  $P''$ ,

$$(V' - V'')/(P' - P'') = - RT/aP'P''. \dots\dots\dots(1)$$

The mean coefficient between  $P'$  and any other pressure  $P$ , is similarly given by  $-RT/aP'P$ , and is  $P''/P$  of that between  $P'$  and  $P''$ , which is directly obtained from the tables if  $V'$  and  $V''$  are tabulated values. The coefficient between  $P'$  and  $P$ , required for finding any intermediate value  $V$  of the volume at  $P$ , is obtained by simply reducing the tabular coefficient in the ratio  $P''/P$ . We thus obtain the following *exact* rule for interpolation.

*Exact Rule for Interpolation of Volumes at Constant Temperature.* If  $V'$ ,  $V''$  are tabular values of the volume at  $T$  corresponding to pressures  $P'$  and  $P''$  (of which  $P''$  is the greater), to find the volume  $V$  at any intermediate pressure  $P$ , find the difference  $V' - V$  by simple proportion, increase it in the ratio  $P''/P$ , and subtract it from  $V'$ .

This operation is very easily performed with a slide-rule, and the result is theoretically exact however great the difference. Applying the rule to the previous example, 2, the difference  $V' - V$  found by simple proportion was 0.2814. This difference is to be increased in the ratio  $P''/P$  or 100/95, which is most easily done by adding  $.2814 \times 5/95$  or .0148, giving .2962, which is subtracted from the volume at 90 lbs., giving  $V = 5.1567$  as the correct result for the volume at 95 lbs., in place of the approximate result 5.1715 found by simple proportion.

**174. The Pressure Coefficient.** The pressure coefficient  $(dP/dT)_V$  at constant volume may be determined, in the case of a gas or vapour, by observing the increase of pressure  $dP$  for a rise

of temperature  $dT$  when the fluid is enclosed in a non-expansive envelope, such as a silica bulb. It is easy in the case of a gas to allow for the expansion of the bulb if necessary by making a small correction to the observed change of pressure. But in the case of a solid or liquid, the correction would be so large and uncertain, that the direct measurement of  $(dP/dT)_V$  may be regarded as impracticable. The required value can however be deduced from those of the expansion coefficient and the compressibility (which can always be determined directly) by means of a simple relation between the partial differential coefficients, which follows immediately from the general expression for the total change of volume in terms of  $P$  and  $T$

$$dV = (dV/dT)_P dT + (dV/dP)_T dP. \dots\dots\dots(2)$$

This relation expresses the obvious fact that any desired change of volume may be made in two steps, first by raising the temperature through the given range  $dT$  at constant pressure, and secondly by raising the pressure while the temperature is kept constant. The final result is independent of the order of the operations, and is the same as if both pressure and temperature were changed simultaneously.

If the expansion due to increase of temperature in the first operation is equal to the compression due to increase of pressure in the second, we have  $(dV/dT)_P dT = - (dV/dP)_T dP$ , and the total change of volume  $dV = 0$ . In other words, when  $dV = 0$ , the relation (2) gives the ratio of  $dP$  to  $dT$  under the condition that  $V$  remains constant, or the value of the coefficient  $(dP/dT)_V$ , thus

$$(dP/dT)_V = - (dV/dT)_P / (dV/dP)_T = - (dP/dV)_T \times (dV/dT)_P \dots\dots(3)$$

A similar relation holds in all cases between the partial differential coefficients of three quantities, such as  $P$ ,  $V$ , and  $T$ , if any one of the quantities may be regarded as a function of the other two. The relation is purely mathematical or formal, depending simply on the definition of the coefficients, and not on the properties of the substance, or on the laws of thermodynamics. But such relations are often very useful in deducing the value of a coefficient like  $(dP/dT)_V$  when it cannot be determined by direct experiment.

**175. Relations between the Partial Differential Coefficients.** If we take only the six quantities  $P$ ,  $V$ ,  $T$ ,  $E$ ,  $H$ ,  $Q$ , there are 20 relations of this type between the partial differential



coefficients, being the number of possible combinations of 6 letters taken 3 at a time. The student need not be dismayed by this, because very few of these relations are commonly required, and any one may be deduced from any other by the simple process of interchanging the letters. Thus if we take the expression for the isothermal elasticity

$$-V(dP/dV)_T = V(dP/dT)_V/(dV/dT)_P, \dots\dots\dots(4)$$

and substitute the letter  $Q$  for  $T$  throughout the relation, we obtain

$$-V(dP/dV)_Q = V(dP/dQ)_V/(dV/dQ)_P, \dots\dots\dots(5)$$

which is the corresponding expression for the adiabatic elasticity.

Taking the ratio of the two elasticities, we obtain the well known result

$$\begin{aligned} (dP/dV)_Q/(dP/dV)_T &= (dQ/dV)_P(dV/dT)_P/(dQ/dP)_V(dP/dT)_V \\ &= (dQ/dT)_P/(dQ/dT)_V, \dots\dots\dots(6) \end{aligned}$$

discovered by Laplace, that for any substance the ratio of the adiabatic to the isothermal elasticity is the same as the ratio of the specific heat  $(dQ/dT)_P$  at constant pressure, to the specific heat  $(dQ/dT)_V$  at constant volume. Between the partial coefficients of six quantities there are 45 relations of this type, which follow from the definition of the coefficients concerned, and are independent of the laws of thermodynamics.

It follows from the last relation, in the case of a gas obeying Boyle's law, for which  $(dP/dV)_T = -P/V$ , that, if the ratio of the specific heats is constant and equal to  $\gamma$ , the equation of the adiabatic is

$$(dP/dV)_Q = -\gamma P/V, \text{ which gives } PV^\gamma = K, \dots\dots\dots(7)$$

In the case of steam, according to the author's equation, the ratio of the specific heats  $S_P/S_V$  is not constant, but is given by the expression

$$S_P/S_V = (n+1)RT/anP(V-b), \dots\dots\dots(8)$$

If however we substitute  $(dP/dV)_T = -aP^2/RT$  in (6), the adiabatic equation becomes

$$(dP/dV)_Q = -\gamma P/(V-b), \text{ which gives } P(V-b)^\gamma = K, (9)$$

where  $\gamma = 1 + 1/n$ .

If we substitute  $H$  and  $Q$  respectively for  $V$  in relation (8), we obtain two others which are often useful, namely,

$$(dH/dP)_T = -(dH/dT)_P(dT/dP)_H = -SC, \dots\dots\dots(10)$$

$$(dQ/dP)_T = -(dQ/dT)_P(dT/dP)_Q = -ST/(n+1)P, \dots\dots(11)$$

These are more fully explained in the following section on the specific heats.

**Example 4.** Find from Table V the value of the pressure coefficient  $(dP/dT)_V$  for steam at  $200^\circ\text{C}$ . and 100 lbs., and compare the result with the value for an ideal gas at the same  $T$  and  $P$ .

The tables give  $(dV/dT)_P = 0.012035$  at  $200^\circ$  and 100 lbs. The value of  $(dV/dP)_T$  is  $-RT/aP^2$ , or  $0.05065$  at the same point. Whence  $(dP/dT)_V = 0.2380$  lb. per sq. in. per  $1^\circ\text{C}$ . For an ideal gas the value is  $P/T$ , or  $0.2113$  (F.P.C.).

The cooling-effect  $(dT/dP)_H$  may be similarly found from Table IV, as explained in § 176. The adiabatic coefficient  $(dP/dT)_Q$  may be found in the same way from Table VI. Its value for steam is  $(n+1)P/T$ , where  $n+1$  is the value of the adiabatic index, which is one of the fundamental properties determined by direct experiment.

**Example 5.** Find the two elasticities and their ratio for steam at  $200^\circ\text{C}$ . at pressures of 100, 200, and 500 lbs.

Pressure lbs./sq. in.	100	200	500
Adiabatic Elasticity	130.42	261.77	662.4
Isothermal Elasticity	96.53	186.20	413.6
Ratio, $\gamma RT/aP(V-b)$	1.351	1.406	1.602

The adiabatic elasticity is given by the expression  $\gamma PV/(V-b)$ , which is very nearly equal to  $\gamma P$ , where  $\gamma = 1 + 1/n = 1.300$ . But the isothermal elasticity given by the expression  $aP^2V/RT$ , is less than  $P$ . The values are easily found at any point from Table V. Those at 500 lbs. refer to the state of supersaturation which commonly occurs in the discharge through a nozzle (Chap. X). The adiabatic elasticity is the coefficient which determines the discharge.

**176. The Specific Heat.** The specific heats are so important from an experimental standpoint that they are commonly denoted by special symbols, such as  $S$  and  $s$  for the vapour and liquid at constant pressure. But they may have very different values under different conditions, and it is often convenient to employ the notation of partial differential coefficients to distinguish other possible varieties of specific heat.

The specific heat is measured theoretically by observing the quantity of heat  $dQ$  required per unit mass to raise the temperature through an interval  $dT$ , and taking the ratio  $dQ/dT$ . If the heat

is supplied under the condition of constant pressure, the experiment gives the specific heat at constant pressure, which is denoted by  $(dQ/dT)_P$ , and is equal to the rate of increase of the total heat  $H$  under the same condition, namely  $(dH/dT)_P$ , as already explained in Chapter II. Similarly the specific heat measured under the condition of constant volume is denoted by  $(dQ/dT)_V$ , and is equal to the rate of increase of the intrinsic energy  $E$  under the same condition, namely  $(dE/dT)_V$ . The quantity actually measured in a calorimetric experiment is generally either the change of total heat  $H$ , or the change of intrinsic energy  $E$ , between the given initial and final states. This is commonly divided by the range of temperature and called the mean specific heat over the range considered and under the given conditions. This method of statement is sufficiently precise for many practical purposes, especially when the experiments are not very accurate. But the relations  $(dQ/dT)_P = (dH/dT)_P$ , and  $(dQ/dT)_V = (dE/dT)_V$ , do not hold accurately except under the conditions of constant  $P$  and  $V$  respectively, and it is often necessary to consider more closely the exact relation between the specific heats and the rates of variation of the total heat and intrinsic energy.

*Variation of Total Heat.* In the case of steam, by far the most important relations are those affecting the variation of the total heat  $H$  with pressure and temperature, which will be considered first as an example of the use of partial differential coefficients. The variation of  $H$  with  $T$  at constant  $P$  is fully determined by the specific heat  $S = (dH/dT)_P$ . Conversely the value of the specific heat at any point defined by  $T$  and  $P$ , is easily obtained from Table IV of the values of  $H$  for superheated steam, by taking differences between any two values at the same pressure and dividing by the range of temperature.

*Example 6.* Find  $S$  at 20, 100, and 500 lbs. and at  $200^\circ$  and  $800^\circ$  C. Find also the mean values over the range  $200^\circ$  to  $800^\circ$  at the same pressures.

The required values of  $S$  at  $200^\circ$  may be obtained to three places of decimals by taking the difference between the tabulated values of the total heat at  $190^\circ$  and  $210^\circ$  C. at the required pressures, and dividing by 20. Similarly at  $800^\circ$ , and  $250^\circ$ , we obtain the following.

Values at $200^\circ$ C.	$S_{20} = .489$	$S_{100} = .537$	$S_{500} = .777$
" $250^\circ$ C.	" .486	" .517	" .671
" $300^\circ$ C.	" .483	" .504	" .608
Mean $200^\circ$ - $300^\circ$ C.	" .4853	" .5174	" .6780

It will be observed that the mean over the range from  $200^{\circ}$  to  $300^{\circ}$  is nearly equal to the value at the mean point  $250^{\circ}$  C. even at high pressures. Values of  $H$  at temperatures intermediate between the tabulated values can be obtained by simple proportion from the relation  $dH = SdT$  at constant pressure, correct to two places of decimals when the temperature interval is  $10^{\circ}$  C. So high an order of accuracy of tabulation may appear at first sight superfluous; but many results depend on small differences of total heat, and require this order of accuracy in the relative values. It is also very convenient to be able to deduce the specific heat at any point to three significant figures.

*Variation with Pressure.* The variation of the total heat with pressure at constant temperature, expressed by the relation  $dH = (dH/dP)_T dP$ , is even simpler in practice than the variation with temperature at constant pressure, because it appears that the coefficient  $(dH/dP)_T$  is constant within the limits of experimental error over the required range at constant temperature. The values of this coefficient multiplied by 10 are given in the third column of Table IV under the heading  $10SC$ , and show the diminution of  $H$  for 10 lbs. increase of pressure at each temperature. Since the coefficient is independent of the pressure, it is very easy to find exact values of the total heat at any pressure intermediate between the tabulated values by simple proportion. But the value of the coefficient  $(dH/dP)_T$  cannot, like that of the specific heat, be determined by direct experiment. It may however be deduced with equal certainty from observations of the cooling-effect  $C$ , and affords another instructive illustration of the relations between the partial differential coefficients.

*Example 7.* Find  $P$  and  $C$  from Table IV, when  $H = 680$  at  $200^{\circ}$  C.  $\phi H = 681.41$  at 100 lbs., and  $10SC = 0.834$  at  $200^{\circ}$  C. Therefore when  $H = 680$ ,  $P = 100 + 1.41 \times 10/0.834 = 116.9$  lbs. Also  $S_{100} = 0.538$ ,  $S_{120} = 0.549$ , whence  $S_{117} = 0.547$ , which gives  $C = 0.834/10S = 0.1525^{\circ}/\text{lb.}$

**177. The Cooling-Effect  $C$ .** The cooling-effect  $C$  is defined as the ratio of the fall of temperature  $dT$  to the fall of pressure  $dP$  when the fluid is expanding under the condition of steady flow at constant total heat, which is approximately realised in practice by a throttling process. When expressed as a partial differential coefficient,  $C$  is accordingly represented by the notation  $(dT/dP)_H$ .

In order to find its relation to the partial derivatives of  $H$  when  $T$  and  $P$  are taken as coordinates, we take the general expression

$$dH = (dH/dT)_P dT + (dH/dP)_T dP, \dots\dots\dots(12)$$

and apply the condition  $dH = 0$ , or  $H = \text{constant}$ , which gives

$$C = (dT/dP)_H = - (dH/dP)_T / (dH/dT)_P. \dots\dots\dots(13)$$

The coefficient  $(dH/dT)_P$  is the specific heat at constant pressure, denoted by  $S$ , but the coefficient  $(dH/dP)_T$  would be very difficult to measure in practice. The coefficient  $C$ , on the other hand, is comparatively easy to measure experimentally by the methods already explained in Chapter III. But since the unknown coefficient  $(dH/dP)_T$  is equal to  $-SC$ , by the above relation, we are enabled to express the complete variation of  $H$  in terms of the known coefficients  $S$  and  $C$  as follows,

$$dH = SdT - SCdP. \dots\dots\dots(14)$$

General expressions for  $dH/dT$  or  $dH/dP$  under any desired conditions are readily obtained by dividing this expression for  $dH$  by  $dT$  or  $dP$  respectively. The general expression for  $dH/dT$  is

$$dH/dT = S - SC(dP/dT), \dots\dots\dots(15)$$

which has different values under different conditions depending on the relation between  $P$  and  $T$  or the value of  $dP/dT$ . Thus if we require to find  $(dH/dT)_V$ , or the rate of increase of  $H$  with  $T$  at constant volume, we have merely to substitute  $(dP/dT)_V$  for  $(dP/dT)$  in the above expression. Similarly to find  $(dH/dT)_s$ , or the rate of increase of  $H$  for saturated steam, we must substitute for  $dP/dT$  the rate of increase of the saturation pressure,  $dp/dt$ , together with the proper values of  $S$  and  $C$  at saturation pressure and temperature. Since  $dp/dt$  is known with considerable accuracy, this relation is very useful in discussing the possible variations of the specific heat and the total heat in the neighbourhood of saturation (see III (7), IV (6), etc.).

*Example 8.* Find the values of  $(dH/dT)_s$  from Table III ( $H$ ) for saturated steam at  $100^\circ$ ,  $120^\circ$ , etc. to  $240^\circ$  C. Verify the results by calculating  $S$  at saturation from the formula

$$S_s = 0.4772 + an(n+1)cp/T,$$

and  $SC(dp/dt)$  from the values of  $SC$  given in Table IV, taking  $(dp/dt) = L_p/4WT$  from Table I.

\* It is important to remember that  $dH/dT$  is not the same as the specific heat  $dQ/dT$ , except under the special condition of constant pressure, when  $dP/dT = 0$ .

Thus at  $100^{\circ}\text{C}$ .

$$S_g = 0.4772 + 0.0246 = 0.5018, \quad C_p = 0.1861/0.5018 = 0.3708,$$

$$SC(dp/dt) = 0.1861 \times 539.8 \times 14.69/40.45 \times 379.1 = 0.0977,$$

whence  $(dH/dT)_g = 0.4041.$

The required values of  $(dH/dT)_g$  may also be obtained to three places of decimals from Table III (*H*), e.g. at  $100^{\circ}\text{C}$ ., by taking the difference between the values of  $H_g$  at  $90^{\circ}$  and  $110^{\circ}$ , and dividing by 20, giving  $8.07/20 = 0.404$ .

These quantities are seldom required in practice, but are of considerable theoretical interest. The same remark applies to the specific heat at constant volume, which is given as a further illustration.

*The Specific Heat at Constant Volume,  $S_V$* , is so seldom required in the theory of the steam-engine that the letter  $S$ , without a suffix, will always be used to denote the specific heat at constant pressure. The suffix  $P$  may be added for constant pressure, if desired, in case there is any possibility of confusion, or in expressions where both specific heats occur. But the suffix  $P$  is unnecessary, even in this case, provided that the suffix  $V$  is employed for constant volume.

The value of the specific heat at constant volume  $S_V$  is readily deduced from that at constant pressure when required by means of the following relations.

In order to find  $(dH/dT)_V$  at constant volume at any given point defined by  $P$  and  $T$ , we have merely to put  $(dP/dT)_V$  in the last relation (15), thus,

$$(dH/dT)_V = S - SC(dP/dT)_V = (dE/dT)_V + aV(dP/dT)_V, \dots (16)$$

since  $H = E + aPV$ . Thus  $(dE/dT)_V$ , the specific heat at constant  $V$ , is given by

$$S_V = (dE/dT)_V = S - (SC + aV)(dP/dT)_V.$$

*Example 9.* Verify the following expressions, if

$$H = a(n+1)P(V-b) + abP + B,$$

and

$$V = RT/aP - c + b,$$

in the case of steam, according to the author's equation.

$$SC = a(n+1)c + ab,$$

whence  $SC + aV = (1 + ancP/RT) RT/P = aT (dV/dT)_P$ ,

$$S = S_0 + an(n+1)cP/T = (n+1)R(1 + ancP/RT) \\ = a(n+1)(dV/dT)_P P/T,$$

$$S_V = nR(1 + ancP/RT)(1 - acP/RT),$$

$$S/S_V = (n+1)/n(1 - acP/RT),$$

$$S - S_V = R(1 + ancP/RT)^2 = S(1 + ancP/RT)/(n+1) \\ = (SC + aV)(dP/dT)_V.$$

When it is required to find an exact value of  $S$  or  $SC$  or  $S_V$  at any particular point, given  $P$  and  $T$ , the calculation is most easily effected by using the expressions above given in terms of the coaggregation volume  $c$ , the values of which are tabulated in Table III (c). But when the value of  $S$  is given, it is better to use the formula for the difference in terms of  $S$ , namely,

$$S - S_V = R(S/S_0)^2, \dots\dots\dots(17)$$

where  $R = 0.11012$ , and  $S_0 = 0.4772$ . The ratio  $S/S_0$  is equal to  $1 + ancP/RT$ . Other useful formulae in terms of  $S$  are

$$SC + aV = 3ST/13P, (dP/dT)_V = SP/S_0T, (dV/dT)_P = 3S/13aP. \\ \dots\dots\dots(18)$$

\* *Example 10.* Given  $S = 0.5373$  at  $200^\circ \text{C}$ . and 100 lbs. pressure, find the ratio and difference of the specific heats.

$$S - S_V = 0.1396, \quad S_V = 0.3977, \quad S/S_V = 1.3510,$$

$$SC + aV = 0.5866, \quad (dP/dT)_V = 0.2380, \quad (dV/dT)_P = 0.012053,$$

all in (F.P.C.) units.

**178. General Expression for the First Law of Thermodynamics.** By the principle of the conservation of energy as applied to heat exchanges, if a small quantity of heat energy  $dQ$  is supplied to a body, part remains in the body as an increase of intrinsic energy  $dE$ , while part is expended in the performance of external work  $dW$ . The increase of intrinsic energy  $dE$  is less than the heat supplied  $dQ$  by the thermal equivalent  $AdW$  of the external work done. This may be expressed by the familiar equation

$$dQ = dE + AdW, \dots\dots\dots(19)$$

in which for convenience the separate terms are expressed in equivalent thermal units per unit mass of the working substance.

In dealing with heat-engines, the only kind of external work

that need be considered is that done by expansion of the working fluid under a uniform hydrostatic pressure,  $P$ . The expression for  $dW$  in this case is  $PdV$ , where  $dV$  is the corresponding increment of volume. In applying this formula to estimate the work done per revolution from an indicator diagram,  $P$  represents the effective pressure, or the excess of the forward pressure over the back pressure at any point of the stroke, while  $dV$  represents an appropriate fraction of the volume swept by the piston. In thermodynamical formulae on the other hand,  $P$  represents the absolute pressure reckoned from zero, and  $V$  represents the volume of unit mass of the substance under the given conditions of temperature and pressure. The product  $PdV$ , representing the work done, is reduced to thermal units per unit mass by a numerical factor, denoted by  $a$ , depending on the units of pressure and volume. The expression of the first law becomes

$$dQ = dE + aPdV \quad \dots\dots\dots(20)$$

If unit mass of the substance is contained in a cylinder and is allowed to expand without supply of heat under the condition  $dQ = 0$ , the expansion is said to be "adiabatic," and is given by the equation  $dE + aPdV = 0$ . The relation between  $P$  and  $V$  in adiabatic expansion may be deduced from this condition if  $E$  is known in terms of  $P$  and  $V$ . Thus in the case of dry steam we have the expression  $E = anP(V - b) + B$ , where  $n$ ,  $b$ , and  $B$  are constants. The expression of the first law in the case of adiabatic expansion may be written

$$ndP(V - b) + (n + 1)PdV = 0, \text{ or } P^n(V - b)^{n+1} = K, \dots(21)$$

where  $n = 10/3$ , and  $K$  is a constant determined by the initial values of  $P$  and  $V$ .

By the first law, when  $dQ = 0$ , we must have  $aPdV = -dE$ , or the thermal equivalent of the work done in adiabatic expansion of unit mass in a cylinder from  $V'$  to  $V''$ , must be equal to the diminution of intrinsic energy  $E' - E''$ . We accordingly obtain the following expression for the work from that already given for the energy,

$$AW = anP'(V' - b) - anP''(V'' - b) = E' - E'', \dots(22)$$

in which the final pressure  $P''$  must be calculated in terms of the initial pressure  $P'$  and the ratio of expansion  $V''/V'$  from the adiabatic equation which gives the condition

$$P''/P' = (V' - b)^{1.2}/(V'' - b)^{1.2}.$$



**Example 11.** Find the work done by unit mass of dry steam in adiabatic expansion from  $P' = 180$  lbs.,  $V' = 8.7501$  cb. ft., to  $V'' = 10.016$  cb. ft. per lb.

Here  $V' - b = 8.7341$ , and  $V'' - b = 10.000$ , whence

$$P''/P' = 0.27787, \quad P'' = 44.46.$$

The thermal equivalent of the work done is 52.41 cal. C.

The expression given above is the work done during expansion after cut-off, and not the whole work done in the cylinder including admission and exhaust. The thermal equivalent of the work done during admission is  $aP'V'$ , that during exhaust is  $-aP''V''$ , if the expansion is complete, or the final pressure  $P''$  is equal to the back pressure. When these two terms are included, we obtain the complete expression

$$AW + aP'V' - aP''V'' = a(n+1)P'(V' - b) - a(n+1)P''(V'' - b) + ab(P' - P''), \dots (28)$$

which is seen to be equal to the drop of total heat,  $H = E + aPV$ .

*Expression for the First Law in terms of H.* For this reason among others, the total heat is more useful in steam-engine work than the intrinsic energy, especially in problems depending on steady flow, as previously explained in Chapter II. The general expression for the first law in terms of  $H$  is also more useful than that in terms of  $E$ . By substituting  $dH = aVdP + aPdV$  for  $dE$  we obtain the expression

$$dQ = dH - aVdP, \dots (24)$$

which supplies a number of useful relations between the specific heat and the total heat, in addition to expressions for the work done and the heat absorbed under various conditions occurring in practice. The equation in this form applies primarily to the case of steady flow, since  $-aVdP$  is the thermal equivalent of the kinetic energy generated in the fluid in steady flow for a drop of pressure  $-dP$ . It shows that when  $dQ = 0$  (i.e. when no heat is supplied externally or generated by internal friction) the change of total heat  $dH$  must be equal to  $aVdP$ .

**179. Effect of Friction.** The expression for the first law in terms of  $H$  is seldom mentioned, and very little use is made of it in purely theoretical works. But it is most important for practical purposes, and it is most useful, in applying the equation in this form, to take account of friction by including heat so generated

in  $dQ$ . The condition  $dQ = 0$  in steady flow is then equivalent to that of constant entropy, and the integral of  $dQ/T$  along any path is the same as the increase of entropy, provided that  $dQ$  includes heat generated by internal friction, so that it is always equal to  $dH - aVdP$ . A great deal of argument has been spent on questions of this kind which appear to turn chiefly on the interpretation given to  $dQ$ . In many books on thermodynamics,  $dQ$  is explicitly restricted to denote heat supplied from external sources, in which case the expression for the first law in the form  $dQ = dE + aPdV = dH - aVdP$  does not apply to cases in which heat is generated by internal friction. If part of the work  $PdV$  is converted into heat by internal friction, the heat so generated remains in the body and goes to increase the internal energy. The work actually done by the fluid in expanding is still represented by  $PdV$ , but is no longer equal to the work utilised externally. Since in experimental work it is always necessary to take the values of  $E$ ,  $P$ , and  $V$ , as those corresponding to the actual or observed state of the fluid, the simplest method of extending the application of the equation to include internal friction is to assume that  $dQ$  represents all heat supplied to the working substance whether by internal friction or from external sources. The properties of the substance are determined by experiments in which friction is either excluded, as in measuring the adiabatic index, or determinate, as in a throttling experiment; so that the extension here employed does not in any way invalidate the application of the equation by making  $dQ$  indeterminate, as might be supposed at first sight. On the contrary, the equation remains true, and becomes available for estimating work wasted in internal friction.

The expression  $aVdP$  represents the thermal equivalent of the work actually done by the pressure drop in generating kinetic energy in the working fluid. In the absence of friction, the whole of this work is theoretically available for driving a vane in a turbine, or generating velocity in a nozzle. But in practice part is necessarily wasted in friction and reconverted into heat. Neglecting external loss or gain of heat, which is often permissible in the case of large engines or turbines,  $dQ$  in the general equation represents work wasted in internal friction, and  $dH$  represents the work utilised, or remaining as kinetic energy of flow.

In the extreme case of a simple throttling process without change of velocity, the whole of the available work is wasted in friction (represented by the generation of heat  $dQ = -aVdP$ ) and

$dH = 0$ , or  $H$  remains constant. At the other extreme, when there is no friction,  $dQ = 0$ , and  $dH = aVdP$ , it being assumed in both cases that there is no *external* heat-loss or gain.

The differential equation represents very closely the case of a reaction turbine in which the expansion is practically continuous. The efficiency of conversion at any stage is the ratio  $dH/aVdP$  of the work utilised to the whole work done, which is readily estimated when the expansion curve, or the relation between  $P$  and  $V$ , is given, or determined by observation. In an impulse turbine a similar expression may be applied to each separate stage of the expansion, by observing the initial and final states in each. If  $P'$  and  $P''$  are the initial and final pressures in any stage, the available work of expansion is first converted into kinetic energy of flow in a nozzle. The kinetic energy generated in this case is nearly equivalent to the adiabatic drop of  $H$  since the expansion is extremely rapid. Part of the kinetic energy is subsequently wasted in friction, so that the actual drop of  $H$  corresponding to the observed final state at  $P''$  is less than the adiabatic drop due to the fall of pressure  $P' - P''$ . The efficiency of the stage considered is the ratio of the actual drop of  $H$  to the adiabatic drop.

*Example 12.* Neglecting  $b$  in the equation for dry steam, find the efficiency at any stage if the actual expansion curve is given by the equation  $PV^\gamma = K$ .

Since  $H = (13a/3)PV + B$ , neglecting  $b$ ,

$$dH/dP = (13a/3)(V + PdV/dP).$$

But  $dV/dP = -V/\gamma P$ , from the given curve, hence the efficiency

$$dH/aVdP = (13/3)(1 - 1/\gamma).$$

Since the effect of friction is always to generate heat at the expense of work, and never the reverse, the actual drop of total heat  $-dH$  can never exceed the equivalent of the available work  $-aVdP$  in any stage if no heat is lost externally. The two are equal in the limiting case of frictionless expansion, when  $\gamma = 1.8$ .

**180. Application to Adiabatic Expansion and Throttling.** It is difficult in practice to supply heat efficiently to the working fluid during rapid expansion. Moreover a quantity of heat supplied during expansion produces less useful effect than an equal quantity supplied before expansion. For both reasons adiabatic processes are most important in the operation of heat-

engines, since rapidity of working is an essential factor in the output of power. On the other hand, in experimental work on the properties of the fluid, slow processes are often required for the avoidance of friction and the attainment of equilibrium of temperature. They may also be postulated in theoretical work for similar reasons. If the condition of no external loss or gain of heat is not satisfied, it is always possible to make allowance for any actual loss or gain by including it in the fundamental equation, and making a suitable correction to the observed heat-drop. If it is desired to distinguish between external heat supply  $Q_x$  and internal friction  $Q_f$ , the general equation may be written in the form

$$dQ_x + dQ_f = dH - aVdP. \dots\dots\dots(25)$$

The following examples are intended to illustrate the methods of integrating the equation for a finite range of expansion in a few ideal cases.

*Example 13.* Find the work available in adiabatic flow from  $P' = 160$  lbs. at  $300^\circ \text{C.}$  to  $P'' = 40$  lbs. (The equations for dry steam apply to this case.)

The integral of  $aVdP$  is found from the adiabatic equation  $P^n (V - b)^{n+1} = K$ , which gives the expression

$$a(n+1)P'(V' - b) - a(n+1)P''(V'' - b) + ab(P' - P''),$$

for the integral, and  $(V'' - b) = (V' - b)(P'/P'')^{0.13}$ , for the final volume. From Table V, App. III,  $V' = 3.7501$ , whence  $V' - b = 3.7341$ , and  $V'' - b = 10.848$ . Substituting these values, the integral is found to be 73.09 cal. C.

The expression for the integral is obviously the same as that for the drop of  $H$ , by the formula  $H = a(n+1)P(V - b) + abP + B$ . The result may be verified by finding the final value of  $H$ , corresponding to  $V'' = 10.864$  at 40 lbs., by interpolation in Table IV, which gives  $H'' = 657.47$ . The initial value of  $H$  at  $300^\circ \text{C.}$  and 160 lbs. is  $H' = 730.55$ , whence  $H' - H'' = 73.08$  cal. C.

As an alternative method, the final temperature may be found from the adiabatic equation in the form  $P/T^{n+1} = K$ , which gives  $T'' = 416.25$ , or  $t'' = 143.15^\circ \text{C.}$  The corresponding values of  $H''$  and  $V''$  are then easily found by interpolation in Tables IV and V. But that of  $V''$  is not required for the solution of the problem.

The easiest method of solving the problem is to find the final value of  $H''$  by interpolation in Table IV from the condition of constant entropy. The final value of  $H$  at 40 lbs. must divide the

interval  $H_{140}$  to  $H_{150}$  in the same ratio as the constant value of  $\phi$  divides the same interval in Table VI; which gives the result  $H'' = 657.47$  as before.

The advantage of using the condition of constant entropy is that it applies with slight modification if the final state of the steam is wet. Thus if the expansion had been continued to 10 lbs., we find from Table II,  $t'' = 89.58^\circ \text{C.}$ ,  $G'' = 13.26$ , and the required value of  $H''$  follows from the formula,  $H'' = T''\Phi' - G''$ , where  $\Phi' = 1.69523$ .

It is instructive as a mathematical exercise to verify the exact correspondence of the formulae, and the consistency of the numerical values given by the tables, when different methods of calculation are employed. But in practice when a numerical result is required, the easiest method would naturally be selected.

**Example 14.** Find the heat generated by friction in a continuous throttling process at constant  $H$  between the same limits of  $P$  starting at  $300^\circ \text{C.}$

When  $H$  is constant, we may employ the expression for  $V$  in terms of  $H$ , namely  $aV = 3(H - B)/13P + 10ab/13$ , which gives for the integral of  $aVdP$  the exact formula

$$3(H - B) \log_e (P'/P'')/13 + 10ab(P' - P'')/13.$$

The constant value of  $H$  is  $730.55$ , and we find the result  $85.42$  cal. C. for the heat generated. If there were no friction, the same quantity of heat supplied externally would suffice to keep  $H$  constant during the expansion, and the external work realised would be the equivalent of the heat supplied during expansion. It follows from the general equation that the work done is always exactly equivalent to the heat supplied in frictionless flow at constant  $H$ , but this condition cannot be realised in practice.

In place of *continuous* throttling through a porous plug or long thin tube, the fluid might first be expanded through an aperture or nozzle with very little friction, and the resulting kinetic energy subsequently converted into heat. The friction in this case would be approximately equivalent to  $73.09$  cal. C. as calculated in the previous example (13) and would exactly suffice to raise  $H$  to its initial value at the final pressure. The final state is the same, but the friction depends on the process employed, and may have any value between the limits  $73.09$  and  $85.42$  cal. C., if no heat is externally supplied.

**Example 15.** Find the heat absorbed and the external work done in frictionless flow at constant temperature,  $t = 300^\circ \text{C.}$ , for the same limits of pressure.

Since  $V = RT/aP - c + b$ , the expression for the integral of  $aVdP$  at constant  $T$  is  $RT \log_e (P'/P'') - a(c-b)(P' - P'')$ , which gives 86.44 cal. C. for the thermal equivalent of the work done, taking  $c - b = 0.0847$  at  $300^\circ \text{C.}$

Since the work done in frictionless flow at constant temperature is equivalent to the increase of the potential  $G$ , the same result may be more easily obtained by taking the difference of the values of  $G$  from Table VII, which gives the result 86.45 cal. C.

To find the heat absorbed, it is necessary by the general equation (25) to add the increase of  $H$  to the integral of  $-aVdP$ . The increase of  $H$  taken from Table IV is 5.19 cal. C., which gives 91.63 cal. C. for the heat absorbed.

The heat absorbed at constant temperature is also equal to the increase of entropy  $\Phi$  multiplied by the absolute temperature  $T$ . This is easily verified by taking the increase of entropy, namely 0.15988 from Table VI, and multiplying it by 573.1, which gives the result 91.62 cal. C.

**Weddle's Rule.** When the process of expansion can be defined by an exact equation for  $V$ , as in the preceding examples, accurate results for the work done can always be obtained by integrating  $aVdP$ . But in experimental work the observations may give an arbitrary curve which cannot easily be represented by any simple formula, or merely a series of isolated points representing intermediate states. In cases of this kind it is necessary to perform the integration by a numerical process in the same way as in finding the mean effective pressure from an indicator diagram. One of the simplest and most accurate numerical methods is that known as Weddle's rule, having been discovered by Thomas Weddle in 1854.

To find the integral of  $aVdP$  (or any similar integral) by this rule, the pressure difference is divided into 6 equal parts. The values of the volume  $V_0$  to  $V_6$  are read from the curve at the points of division, and the integral is given by the formula

$$a(P_0 - P_6) (V_0 + 5V_1 + V_2 + 6V_3 + V_4 + 5V_5 + V_6)/20.$$

**Example 16.** In order to test the accuracy of the rule, take the values of the volume at  $300^\circ \text{C.}$  from Table V, at 160, 140, 120, 100, 80, 60, and 40 lbs., and apply the formula. The result found is

86.46 cal. C., which agrees with that found by direct integration, showing that Weddle's rule is very accurate in a case of this kind.

*Example 17.* As a further illustration of Weddle's rule (including a useful exercise in interpolation) find the required values of  $V$  at the same pressures under the conditions  $H$  constant, and  $\Phi$  constant, respectively, starting from 300° C., and deduce the value of the integral of  $aVdP$ . Thus to find the value of  $V$  at  $P = 40$  lbs. and  $\Phi' = 1.65523$ , take the ratio  $\Phi' - \Phi_{140}$  to  $\Phi_{150} - \Phi_{140}$ , namely,  $390/1239$  from Table VI, and multiply it by the difference  $V_{150} - V_{140}$ , namely 0.290, from Table V. Add the result, namely 0.091 to  $V_{140}$ , giving  $V = 10.864$ . Proceeding in this way we find the following values of  $V$  at constant  $\Phi$ ,

$P$	=	160	140	120	100	80	60	40
$V_{\Phi}$	=	3.7501	4.1540	4.6753	5.3765	6.3808	7.9574	10.864

which on applying Weddle's rule give the integral of  $aVdP$  as 78.09 cal. C. as in Ex. 13. Similarly at constant  $H$  we find the following values of  $V$  at the same pressures,

$V_H$	=	3.7501	4.2840	4.9961	5.9927	7.4877	9.9797	14.964
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which give 85.44 cal. C. for the integral of  $aVdP$  at constant  $H$ . Both of these verify the previous results of direct integration so exactly that it is evident that Weddle's rule may be applied with confidence in cases where analytical integration is impossible.

In the majority of tables of the properties of steam, the values of  $H$  and  $\Phi$  are deduced from experimental values of the specific heat by a numerical process of integration, and those of  $V$  are based on independent observations of the volume. The results are necessarily to some extent inconsistent owing to experimental errors, which lead to material discrepancies in the practical use of the tables, especially in applying the laws of thermodynamics to experimental tests. The fundamental relation  $dH = aVdP$ , expressing the application of the first law to adiabatic flow, cannot be satisfied with any approach to accuracy. For example, Peabody's Tables\* (1912) are among the best known, and have been recently

\* The tables of Marks and Davis are based on the same methods as those of Peabody, and show similar discrepancies. If derivatives, such as the specific heat  $S$ , are compared in place of comparing integrals or primitives, such as  $H$ , the discrepancies from the laws of thermodynamics may exceed 20 per cent. especially near the limits of the experimental range. Prof. H. N. Davis (*Engineering*, vol. 102, p. 233, Sept. 8, 1916) has recently argued that such discrepancies cannot be avoided because they arise from the old difficulty of reconciling the expressions for  $H$  and  $V$ . Taking the author's expressions for  $H$  and  $V$ , he has endeavoured to show that the

revised in accordance with the latest German experiments. The value of the adiabatic heat-drop from 160 to 40 lbs. at  $\Phi = 1.69$ , taken from Peabody's Tables, is 131.5 B.Th.U. or 73.05 cal. C., which agrees closely with that above given, Ex. 13.<sup>o</sup> But the integral of  $aVdP$  over the same range is 132.8 B.Th.U. by Weddle's rule, showing a discrepancy of 1 per cent. In many cases the discrepancies are much larger, and lead to serious trouble in practice (see *Engineering*, June 9th, 1916).

*Example 18.* Find the efficiency  $f$  of conversion at any stage for dry steam if the expansion curve is given by the formula  $P(V-b)^{1.2} = K$ . Find the efficiency for each 20 lbs. drop of pressure from 160 to 40 lbs., starting at 300° C., and deduce the overall relative efficiency  $F$  in terms of the adiabatic heat-drop.

The actual efficiency  $f$  at any point, given by the formula  $dH/aVdP$  (see Ex. 12 above), is  $(13/3)(2/12) + 5b/18V$ , and is constant throughout the expansion if  $b$  is neglected. The values of  $H$  at each point may be obtained from those of  $V$  by interpolation in Tables IV and V, or directly from the expression for  $H$ . The integral of  $aVdP$  between any limits, when the index is 1.2, is obtained from the formula

$$6aP'(V'-b) - 6aP''(V''-b) + ab(P' - P'').$$

resulting values of the *second* derivative  $(d^2V/dT^2)_p$  cannot be reconciled with the expression for the *variation* of  $S$  deduced from  $H$ . This method, depending on *second* derivatives, would be admirably adapted to exaggerate the apparent importance of small discrepancies in a vivid fashion. Unfortunately (as the editor of *Engineering* points out in a footnote), Prof. Davis has omitted to notice that his first expression for  $S$  deduced from  $V$  gives the result for the variation of  $S$  in mechanical units, whereas that deduced from  $H$  is naturally expressed in thermal units. The omission of the numerical reduction factor from mechanical to thermal units inevitably leads to the discovery of discrepancies which have no real existence. In reality the agreement of the author's expressions for  $H$  and  $V$  with both laws of thermodynamics is mathematically exact, so that no discrepancies of the kind suggested can possibly arise in any mathematical manipulation provided that the work is correctly performed. The agreement necessarily extends to all the thermodynamical relations between the derivatives, and numerical results for the same quantity deduced from different relations must always inevitably agree within the limits of error imposed by the number of significant figures employed in the calculation. Seeing that the old difficulty of reconciling the expressions for  $H$  and  $V$  with the laws of thermodynamics has been completely solved by the author's method, which was fully explained in 1900, it would appear to be a very retrograde step at the present time to revert to the inconsistent empirical expressions employed by Prof. Davis. The employment of consistent thermodynamical expressions has the further advantage of smoothing out most of the purely experimental errors in the observations on which the numerical results are based.



The ratio of the heat-drop for each 20 lbs. to the corresponding value of the integral is nearly constant, agreeing with the ratio  $dH/aVdP$  within the limits of numerical error of calculation, as shown in the following table. But the overall relative efficiency  $F$ , obtained by taking the ratio of the actual heat-drop to the adiabatic heat-drop 73.09, is appreciably higher, because the work obtainable in frictionless expansion is less than that actually done by the fluid along the assumed path including work done against friction. Part of the heat generated by friction in the early stages is utilised in the later stages, so that the whole of the work expended in friction is not completely wasted. The advantage thus gained by subdivision of the expansion into stages is more marked the lower the efficiency of a single stage, and the greater the range of expansion.

The results are summarised in the following table.

$P$	160	140	120	100	80	60	40
$V$	3.7501	4.190	4.762	5.540	6.670	8.471	11.870
$dH/aVdP$	0.7234	0.7233	0.7231	0.7230	0.7229	0.7227	0.7226
$H$	730.55	724.63	717.98	710.34	701.35	690.20	675.40
$H$ -drop	5.92	6.65	7.64	8.99	11.15	14.80	
$jaVdP$	8.17	9.20	10.58	12.41	15.45	20.49	
Ratio	0.724	0.723	0.722	0.724	0.722	0.722	
Mean efficiency $f$ , 160 to 40 lbs. = $55.15/76.30 = 0.7228$ .							
Overall relative efficiency $F = 55.15/73.09 = 0.7546$ .							

The above is an ideal example intended to illustrate the theoretical relations. In practice the efficiency is usually lower, especially in the early stages, and is not so nearly constant during the expansion. For additional examples, especially in the case of wet steam, see Chapter XII.

**181. General Expression for the Specific Heat.** The fundamental relation  $S = (dH/dT)_P$ , for the specific heat at constant pressure  $(dQ/dT)_P$ , is a special case of a more general expression for the specific heat under any condition in terms of the variation of the total heat  $dH/dT$  taken under the same condition. The required expression follows directly from the general equation for the first law in terms of  $H$ , by dividing the equation by  $dT$ , thus

$$dQ/dT = dH/dT - aVdP/dT, \dots\dots\dots(26)$$

in which it is understood that both  $dH/dT$  and  $dP/dT$  must be taken under the same condition as that for which  $dQ/dT$  is required. For the specific heat at constant pressure  $dP/dT = 0$ , and

$$(dQ/dT)_P = (dH/dT)_P.$$

Similarly for the specific heat at constant volume we obtain

$$(dQ/dT)_V = (dH/dT)_V - aV (dP/dT)_V. \dots\dots\dots(27)$$

Unless the value of  $(dH/dT)$  under the required condition is known, it is necessary to make a further substitution for  $dH/dT$  from (15) in terms of  $S$  and  $C$ . The value of  $(dH/dT)_V$ , for instance, is  $S - SC (dP/dT)_V$ , which gives finally

$$(dQ/dT)_V = S - (SC + aV) (dP/dT)_V. \dots\dots\dots(28)$$

*Saturation Specific Heat of Steam.* The most interesting application of the general formula (26) is to the case of saturation, for which  $dp/dt$  is known from observation of the saturation pressure  $p$ . The value of  $dH/dT$  is generally taken from some empirical formula for the total heat at saturation, such as that of Regnault, which gives  $(dH/dT)_s = 0.305$ ; but better results may be obtained by calculating the value in terms of  $S$  and  $C$  from  $S - SC (dp/dt)$ , as already explained, § 177. The specific heat in question represents the quantity of heat required per degree rise of temperature to maintain unit mass of steam in the dry saturated state when the pressure is increased simultaneously with the temperature at the rate  $dp/dt$ . The specific heat measured under this condition is called for brevity, the saturation specific heat, and denoted by  $(dQ/dT)_s$ . The required value of  $V$  in the formula is the volume of dry saturated steam  $V_s$  at the temperature considered. The formula becomes

$$(dQ/dT)_s = (dH/dT)_s - aV_s (dp/dt). \dots\dots\dots(29)$$

Taking the numerical values from the tables at  $100^\circ \text{C.}$ , namely,  $(dH/dT)_s = 0.404$ ,  $V_s = 26.79$ ,  $dp/dt = 0.525$ ,  $a = 144/1400$  in F.P.C. units, we find the curious result

$$(dQ/dT)_s = 0.404 - 1.447 = -1.043,$$

or the specific heat of steam at  $100^\circ \text{C.}$ , when maintained in the state of saturation, is *negative* and numerically greater than that of water. This is interesting historically as being the first and most important new result obtained by Rankine and Clausius in 1850 by the application of the mechanical theory to steam.

The meaning of this result may be explained as follows. When saturated steam is expanding under the condition of steady flow, the term  $aV_s (dp/dt)$ , representing the thermal equivalent of the external work done per degree fall, will be equal to the drop of total heat  $dH/dT$  per degree, if no heat is supplied by friction or

otherwise. But its numerical value 1.447 at 100° C. is much greater than the drop of total heat 0.404 for dry saturated steam per degree fall. The steam will therefore become wet, or partially condense, unless heat is supplied at the rate + 1.043 cal. per degree fall. Conversely, if dry saturated steam at 100° C. is compressed, heat must be abstracted from it at the rate - 1.043 cal. per degree rise to keep it saturated, otherwise it will become superheated.

**182. Specific Heat of Water.** The specific heat of water when heated under an increasing pressure equal to that of saturation, is commonly taken as being equal to the specific heat at constant pressure  $(dh/dt)_p$ , or else to the rate of increase of the total heat  $h$  under saturation pressure  $(dh/dt)_s$ . Neither of these assumptions is strictly correct. The exact expression for the specific heat of water  $(dq/dt)_s$  in the state of saturation is the same in form as that for steam, and is deduced in the same way with the substitution of  $v$  and  $h$  for  $V$  and  $H$ , thus

$$(dq/dt)_s = (dh/dt)_s - av_s(dp/dt). \dots\dots\dots(30)$$

The quantity most easily measured by Regnault's method in the case of water above 100° C. is  $h_s$ , the total heat under saturation pressure, from which the value of  $(dh/dt)_s$  may be deduced by differentiation. The required value of the specific heat  $(dq/dt)_s$  may then be obtained by subtracting  $av_s(dp/dt)$ , which is accurately known. Taking  $v_s = .01671$  cu. ft. per lb., the value of this term is only .00090 at 100° C., which is an almost negligible fraction of the specific heat, but it becomes more important at high pressures, amounting to .0089 at 200° C. It must also be taken into account in order to render the formulae thermodynamically consistent, especially in the deduction of the entropy of the liquid, where it is commonly neglected (see Chap. VII, § 66).

If we take the difference between the two equations for the saturation specific heats of steam and water, observing that  $H_s - h_s = L$ , the latent heat of vaporisation, and substituting  $L/T$  for  $a(V - v)_s(dp/dt)$  by Clapeyron's equation (Second Law) we obtain the equation as originally given by Clausius

$$(dQ/dT)_s - (dq/dt)_s = dL/dT - L/T, \dots\dots\dots(31)$$

which is commonly employed in estimating the saturation specific heat of steam, and may be directly deduced by applying the first and second laws to a simple cycle of infinitesimal range  $dt$ . But the equation in this form does not afford any clue to the saturation

specific heat of the liquid, and the separate expressions for the saturation specific heats (though not given by Clausius) are in other ways more instructive, because they follow quite simply from the first law, and are independent of the second.

• From the expression (20) for the first law in terms of the intrinsic energy, we may also obtain a general expression for  $dQ/dT$  in terms of  $dE/dT$ , thus

$$dQ/dT = dE/dT + aP/dT. \dots\dots\dots(32)$$

But this is less useful than the corresponding expression in terms of  $dH/dT$ , especially in the case of steam, because it involves coefficients which are seldom required, and difficult to measure.

### 183. General Expression for $dQ$ in terms of $P$ and $T$ .

If we write down the general expression for the variation of  $Q$  in terms of  $P$  and  $T$ , namely,

$$dQ = (dQ/dT)_P dT + (dQ/dP)_T dP \dots\dots\dots(33)$$

we observe that the first coefficient is simply the specific heat  $S$  at constant pressure, but the second coefficient  $(dQ/dP)_T$ , representing the heat absorbed per unit increase of pressure at constant temperature, or more briefly the latent heat of compression, is less familiar and more difficult to measure experimentally. If, however, we substitute from (14) for  $dH$  in terms of  $S$  and  $C$  in the expression  $dQ = dH - aVdP$  for the first law, we find

$$dQ = SdT - (SC + aV) dP. \dots\dots\dots(34)$$

Comparing this with the first expression for  $dQ$ , we observe that the latent heat of compression  $(dQ/dP)_T$  must be equal to  $-(SC + aV)$ , and is easily found from the known values of  $S$  and  $C$ . The negative sign implies that heat will in general be evolved in isothermal compression, unless  $SC$  is negative and greater than  $aV$ , as is the case for water at temperatures below  $4^\circ \text{C}$ .

It will be observed that although both  $E$  and  $Q$  are quantities of energy measurable in calories per unit mass, there is a most essential difference in their definition. The intrinsic energy  $E$  is the quantity of energy actually existing in a body per unit mass in a given state reckoned from a standard state taken as defining the zero of  $E$ . The value of  $E$  reckoned in this way is a *property of the substance*, which has a definite value for every state of the substance, and is always the same for any given state. The change of  $E$  in passing from any given state to any other given state depends

only on the initial and final states and is independent of the process of transformation from one state to the other. On the other hand, the quantity of heat-energy  $Q$  supplied per unit mass in any transformation from one state to another depends essentially on the process by which the transformation is effected, since it includes the external work done in addition to the change of intrinsic energy. The external work done in transforming a substance from a state defined by  $P'V'$ , to a state  $P''V''$  will have different values if the transformation is effected in different ways. Thus if the substance is first heated at constant volume until the pressure is raised from  $P'$  to  $P''$ , and then expanded at constant pressure  $P''$  from  $V'$  to  $V''$ , the work done will be given by the expression  $P''(V'' - V')$ . But if it is first expanded at constant pressure  $P'$  from  $V'$  to  $V''$ , and then heated at constant volume  $V''$  to the same final pressure  $P''$ , the work done will be  $P'(V'' - V')$ . There is an infinite variety of possible cases, each giving different values of  $Q$ .

184. \*Condition for an Exact Differential. The mathematical distinction between  $E$  and  $Q$  is equally definite. Since  $E$  has a definite value in every state of the substance, it is theoretically capable of expression as a function of any two co-ordinates, such as  $P$  and  $T$ , defining the state. The same is true of  $H$ , since it differs from  $E$  only by the term  $aPV$ , which also has a definite value in every state. Taking the case of  $H$  as an example, this implies a simple relation between the partial coefficients  $(dH/dT)_P$  and  $(dH/dP)_T$ , both of which must be derivatives of the same function representing  $H$ . Since the order of partial differentiation is immaterial, we shall obtain identically the same result if we differentiate  $(dH/dT)_P$  with regard to  $P$  at constant  $T$ , as if we differentiate  $(dH/dP)_T$  with regard to  $T$  at constant  $P$ . Denoting the partial coefficients of  $H$  by  $S$  and  $-SC$  respectively, as shown in (14), we obtain the simple and exact relation

$$(dS/dP)_T = - (dSC/dT)_P, \dots\dots\dots(35)$$

which is the necessary and sufficient condition that  $dH$  should be an exact differential, or that  $H$  should be expressible as a function of the coordinates  $P$  and  $T$  defining the state, and should be a property of the substance depending only on the state and independent of the process by which the state has been reached.

Even if we cannot find an exact expression for  $H$  itself in the case of any substance, the above relation between  $S$  and  $SC$  still

holds, and is capable of supplying useful information. Thus if  $S$  is independent of  $P$ ,  $dS/dP = 0$ , and it follows that  $SC$  must be independent of  $T$ ; or if  $S$  is constant, as assumed by Zeuner for steam,  $(dC/dT)_P$  must be zero, or  $C$  must be a function of the pressure only. Conversely, if  $SC$  varies with temperature at constant pressure, as was found to be the case for steam, it follows that  $S$  must show a corresponding variation with pressure at constant temperature. This deduction has been described by some writers as though it was purely a theoretical speculation, requiring experimental verification by direct measurement of  $S$  at various pressures. But it rests only on the first law of thermodynamics, so that, if it had not been verified by experiment, there would have been grave reason to suspect that the experiments were wrong.

*Example 19.* As a further example of the information obtainable from the condition that  $dH$  must be an exact differential, we may take the following relations quoted in Chapter IV (7), which determine the possible variation of the coefficients  $S$  and  $SC$  along a line of constant  $H$ .

$$C(dS/dT)_H = (dS/dP)_H = (dS/dP)_T + C(dS/dT)_P = S(dC/dT)_P, \quad \dots\dots(36)$$

The first of the above relations follows from the definition of  $C$ . The second follows from the general expression for the variation of  $S$  in terms of  $P$  and  $T$ . The third follows by substituting for  $(dS/dP)_T$  its equivalent  $-(dSC/dT)_P$  from the condition (35) that  $dH$  is an exact differential. The last expression shows that if  $(dC/dT)_P = 0$ , or if  $C$  is a function of the pressure only, both  $dS/dT$  and  $dS/dP$  must also vanish when  $H$  is constant; in other words  $S$  must be constant along a line of constant  $H$ , or must be expressible as a function of  $H$ .

Similarly if we take the corresponding relations for  $SC$ , namely,

$$C(dSC/dT)_H = (dSC/dP)_H = (dSC/dP)_T + C(dSC/dT)_P = S(dC/dP)_T, \quad \dots\dots(37)$$

which are obtained exactly in the same way as those for  $S$ , we observe that if  $(dC/dP)_T = 0$ , or  $C$  is a function of  $T$  only,  $SC$  must be constant at constant  $H$ . This relation has many useful applications in practice.

A precisely similar relation holds between the partial derivatives of  $E$ , or  $V$ , or any property of a substance depending only on the state. But a relation of this kind cannot be satisfied by the deri-

vatives of  $Q$ , though they have definite values, namely  $S$  and  $-(SC + aV)$  respectively, in any given state, because  $Q$  itself cannot be expressed as a function of the coordinates defining the initial and final states, unless the process of transformation from one state to the other is given. The general expression for  $dQ$  differs from  $dH$  by the term  $-aVdP$ , which cannot be integrated unless  $V$  is given as a function of  $P$ , i.e. unless the process of transformation is defined. This may be expressed by saying that  $dQ$  is *not* an exact differential, because the necessary condition

$$(dS/dP)_T = -(d(SC + aV)/dT)_P$$

cannot be satisfied if condition (35) holds in the case of  $H$ . But although  $dQ$  itself cannot be an exact differential, so that  $Q$  cannot be tabulated as a property of the substance, it is possible to find a closely related function called the Entropy, which serves the same purpose.

**185. Expression for the Entropy  $\Phi$ .** An expression of the form given for  $dQ$  by the first law, namely,

$$dQ = SdT - (SC + aV)dP, \dots\dots\dots(34)$$

can always be converted into an exact differential by multiplication by an appropriate factor. If  $X$  is the required factor, the value of  $X$  is determined by the condition already given for an exact differential, which reduces in the present case, remembering that  $(dS/dP)_T = -(dSC/dT)_P$ , to the form

$$S(dX/dP)_T + (SC + aV)(dX/dT)_P + aX(dV/dT)_P = 0. \dots(38)$$

Since it is essential that the differential  $XdQ$  of the new function should be simply related to  $dQ$ , we require only the simplest possible value of  $X$  satisfying this condition. Applying the condition to the case of an ideal gas, for which  $C = 0$ , and  $(dV/dT)_P = V/T$ , we have the simple solution,  $X = 1/T$ . It follows from Carnot's principle that the integrating factor  $X$  must be the same for all substances, and must be a function of the temperature only.

Putting  $1/T$  for  $X$  in the above condition (38), we obtain the relation

$$(dQ/dP)_T = -(SC + aV) = -aT(dV/dT)_P, \dots\dots\dots(39)$$

as a general expression of Carnot's principle, or the second law of thermodynamics, in a form *applicable to all substances*. The relation in this form is also the direct expression of the condition that  $XdQ$  or  $dQ/T$  should be the exact differential of some function  $\Phi$

of the coordinates  $P$  and  $T$  defining the state. The function  $\Phi$  is called the Entropy, and is a property of the substance capable of tabulation for any temperature and pressure, like the total heat. The entropy  $\Phi$  is the property which remains constant in an adiabatic transformation when no heat is supplied by friction or otherwise, and is therefore extremely useful in the theory of heat-engines, where adiabatic processes play such an important part.

The general expression for the entropy of any substance is obtained by integrating the expression for  $d\Phi$  or  $dQ/T$ , namely,

$$d\Phi = dQ/T = SdT/T - a(dV/dT)_P dP, \dots\dots\dots(40)$$

which is necessarily an exact differential if the expressions for  $S$  and  $(dV/dT)_P$  are chosen to satisfy the two conditions given by the first and second laws. These conditions can be expressed in a great variety of ways in terms of other variables, such as  $V$  and  $T$ , or  $P$  and  $V$ . Some of the simplest and most useful of the resulting relations are collected in the following section.

*Example 20.* Verify that the expression above given for  $dQ/T$  is an exact differential.

We have evidently,  $(d\Phi/dT)_P = S/T$ , and

$$(d\Phi/dP)_T = -a(dV/dT)_P.$$

These must satisfy the condition

$$(1/T)(dS/dP)_T = -a(d^2V/dT^2)_P.$$

But this is identical with the condition

$$(dS/dP)_T = -aT(d^2V/dT^2)_P,$$

obtained from the expression for  $dH$  by substituting

$$aT(dV/dT)_P = aV$$

for  $SC$ , from (39).

*Example 21.* If  $H = a(n+1)P(V-b) + abP + B$ , and  $V = RT/aP - c + b$ , find the condition to be satisfied by the expression for  $c$  as a function of  $T$ .

From the expression for  $H$ , we have  $S = a(n+1)P(dV/dT)_P$ . But from that for  $V$  we obtain,  $(dV/dT)_P = R/aP - (dc/dT)_P$ , so that  $S = (n+1)R - a(n+1)P(dc/dT)_P$ . If  $c$  is a function of  $T$  only,  $(dS/dP)_T = -a(n+1)(dc/dT)_P$ . But this must be equal to  $-aT(d^2V/dT^2)_P$  or  $+aT(d^2c/dT^2)_P$ . Which gives for  $c$  the differential equation

$$T(d^2c/dT^2) = (n+1)(dc/dT), \dots\dots\dots(41)$$

the solution of which is of the form  $c = kT^{-n} + b'$ , where  $k$  and  $b'$



are constant. This method\* gives the right value of the index  $n$  representing the variation of  $c$  with temperature, but it leaves the constant  $b'$  undetermined.

A more direct method is to substitute for  $V - b$  in the expression for  $H$ , which gives for  $(dH/dP)_T$  the expression  $-a(n+1)c + ab$ . But this must be equal to  $-aT(dV/dT)_P + aV$ , which gives the condition  $T(d\delta/dt) = -nc$ , showing that the only solution possible is  $c = kT^{-n}$ , if  $c$  is a function of  $T$  only.

If  $c$  may be a function of both  $P$  and  $T$ , the condition to be satisfied, as explained in Chapter III, § 26, is that  $cP/T$  must be some function of  $P/T^{n+1}$ , but the form of the function remains indeterminate.

*Example 22.* Integrate the expression for  $d\Phi$  with the values of  $S$  and  $V$ , given by the condition  $c = kT^{-n}$ .

The expression for  $\Phi$  is given in Chapter VII, equation (13). That for  $d\Phi$  may be verified by differentiation of  $\Phi$ .

**186. Integration of the Expressions for  $H$ ,  $\Phi$ , and  $E$ .** The values of  $H$  and  $V$  at any temperature and pressure can be determined by direct observation, but those of the entropy  $\Phi$  can be deduced only by calculation. The method usually employed in tabulating values of  $\Phi$  is a numerical process of integrating  $(S/T) dT$  at each constant pressure, starting from assumed values at the saturation point. This process necessarily gives results for  $\Phi$  consistent with those for  $H$  if the same tables of  $S$  are employed for both. But since no account is taken of the term  $a(dV/dT)_P dP$  in the expression (40) for  $d\Phi$ , the values of  $\Phi$  obtained are very likely to be inconsistent with those of  $V$ , and may not satisfy the fundamental relation  $-(d\Phi/dP)_T = a(dV/dT)_P$  required by the second law.

In the Tables of Marks and Davis for instance, the values of  $H$  and  $\Phi$  reckoned from saturation appear to be based solely on tables assumed to represent the variation of the specific heat, without direct reference to Linde's equation, which is assumed for the volume. Thus the difference at 200° C. between the values of  $\Phi$  tabulated by Marks and Davis at 80 and 200 lbs. is 0.1177 which

\* This is merely the inverse of the method adopted (R. S., 1900) in deducing the expression for  $H$  from that for  $V$  on the assumption that  $c$  was of the form  $kT^{-n}$ . Prof. Davis (loc. cit.) recently adopted the same method in the endeavour to show that the two expressions for  $H$  and  $V$  were inconsistent. He would naturally have failed to find any inconsistency but for his mistake in omitting a numerical factor.

agrees closely with the difference 0.1175 given by the author's equation. But the value of the same difference obtained by integrating  $a(dV/dT)_P dP$  from Linde's equation is 0.1239, showing a discrepancy of 5 per cent. Similarly at 250° C. the difference between the tabulated values of  $\Phi$  at 200 and 500 lbs. is 0.121, but the value calculated from Linde's equation is 0.1578, showing a discrepancy of 30 per cent. So large a discrepancy, obtained by extrapolating Linde's formula beyond the experimental range, would no doubt be excusable if there were no laws of thermodynamics, and if Prof. Davis had not employed the same extrapolation of Linde's formula (Chapter VI, § 57) by an erroneous method to demonstrate that his extrapolated values of the specific heat in the neighbourhood of 500 lbs. were more reliable than the experimental values directly measured by Thomas.

The simplest analytical method of deducing an expression for  $\Phi$  consistent with the second law, is to assume (1) an expression for  $S_0$  (the specific heat at some convenient standard pressure  $P_0$ ), as a function of  $T$ , and (2) a suitable form of characteristic equation for  $V$  in terms of  $P$  and  $T$ . The value of  $\Phi$  at any point  $P, T$ , is then easily obtained in terms of the standard value  $\Phi_0$  at  $P_0, T_0$ , by integrating  $(S_0/T) dT$  from  $T_0$  to  $T$  at constant pressure  $P_0$ , and adding the integral of  $-a(dV/dT)_P dP$  at constant temperature  $T$  from  $P_0$  to  $P$ . This method may appear at first sight to neglect the variation of  $S$  with pressure, but in reality it takes exact account of this variation in a manner consistent with the fundamental relation  $(dS/dP)_T = -aT(d^2V/dT^2)_P$ , because it is tacitly assumed in the process that  $d\Phi$  is an exact differential. A consistent expression for  $H$  is readily obtained by integrating the expression for  $dH$  on the same assumptions. The values of the constants in the expressions for  $S_0$  and  $V$  may then be determined to satisfy all the experimental data, such as those for  $S$ , and  $C$ , and  $H$ , and  $V$ , and  $p$ , and  $L$ , as closely as possible over the experimental range. If this cannot be done satisfactorily, the forms of the expressions chosen for  $S_0$  and  $V$  must be modified. It is theoretically possible to represent any experimental data within the limits of error of observation by making the expressions sufficiently complicated, but it is most important in practice to keep the relations as simple as possible by choosing expressions of a suitable form. Except in the neighbourhood of the critical point, very simple expressions for  $S_0$  and  $V$  will generally suffice. In many cases, complications which have been introduced with the object

of representing a particular series of experiments with extreme accuracy, are found on further investigation to be irreconcilable with other properties of the substance, and to be due to experimental errors in the original observations.

If an expression of the form  $V = F(P, T)$ , giving  $V$  explicitly as a function of  $P$  and  $T$ , cannot be found to fit the observations, the procedure next in point of simplicity is to express  $P$  in the form  $F(V, T)$  as a function of  $V$  and  $T$ . The corresponding expressions for  $dE$  and  $d\Phi$  in terms of  $S_0$  and  $(dP/dT)_V$  may then be employed; but the expressions obtained for  $H$ ,  $S$ ,  $C$ , and  $(dV/dT)$  are much less convenient than in the previous case. No form of characteristic equation has yet been found capable of representing all the properties of both liquid and vapour. Many of the equations which have been proposed cannot be integrated for both  $H$  and  $\Phi$  in finite terms, and are otherwise objectionable even when apparently simple. But it is generally possible to find simple integrable expressions to satisfy the experimental data with sufficient accuracy over the limited range required in practice.

The following table contains some of the assumptions which have been made for  $S$  and  $V$ , together with the corresponding terms in the expressions for  $H$ ,  $\Phi$ , and  $E$ . The various terms in the first column may be combined in many different ways. The corresponding expressions for  $H$ ,  $\Phi$ , and  $E$ , are obtained by adding the corresponding terms in the other columns, together with a constant of integration, which is determined by substituting the known value of the quantity required at some standard temperature and pressure. It is convenient to take  $S_0$  as the limiting value of  $S$  at zero pressure, which gives  $S_0 - R$  for the specific heat at constant volume. The letter  $k$  stands for any constant, and  $c$  for a volume varying as  $T^{-n}$ .

Table. Expressions for  $H$ ,  $\Phi$ , and  $E$ , on various assumptions.

Assumed	$H$	$\Phi$	$E$
$S_0 = \text{constant}$	$S_0 T$	$S_0 \log_e T$	$(S_0 - R) T$
$+ kT$	$kT^2/2$	$+ kT$	$+ kT^2/2$
$+ k'/T$	$+ k' \log_e T$	$- k'/T$	$+ k' \log_e T$
$V = RT/aP$	0	$- R \log_e P$	0
$+ b$	$+ abP$	0	0
$- c$	$- a(n+1)cP$	$- ancP/T$	$- ancP$
$- ck''P^{m-1}$	$- a(n+1)ck''P^{m/n}$	$- anck''P^{m/n}/T$	$- ack''P^{m/n}(n+1-m)$
$aP = RT/(V-b)$	$+ bRT/(V-b)$	$+ R \log_e (V-b)$	0
$- cRT/V^2$	$- (n+1)cRT/V$	$- (n-1)cR/V$	$- ncRT/V$

**Example 23.** Find expressions for  $H$ ,  $\Phi$ , and  $E$ , from Zeuner's equation.

In this case,  $S_0 = 0.4805$ ,  $a = 1/424$ ,  $ck'' = 192.5$ ,  $n = 0$ , and  $m = 1/4$ .  $H = 0.4805T - 1.816P^{1/4} + B$ , and

$$\Phi = 0.4805 \log_e T - 0.1201 \log_e P + \Phi_0.$$

**Example 24.** Find corresponding expressions from Linde's equation.

In this case,  $n = 3$ ,  $m = 2$ ,  $k'' = 0.02$  (K.M.C.),  $b = 0.0052$ ,  $c = 0.031$  at  $100^\circ \text{C}$ .,  $a = 10,000/427$ ,  $R = 0.1103$ , and  $S_0$  may be taken as desired (VI (16)).

**Example 25.** Find an expression for  $C$  from Rankine's equation for  $\text{CO}_2$ , namely,  $aPV = RT - cRT/V$ , taking  $S_0$  constant and  $\varphi = 2$  (VIII (16)).

The required expressions for  $S$  and  $S''$  are obtained by differentiating the expression for  $H$  given by the above table.

**Example 26.** Find  $H$ ,  $\Phi$ , and  $E$  from Van der Waals' equation, VIII (27).

**187. Thermodynamical Relations depending on the Second Law.** From the expression (39) above given for  $SC + aV$  or  $(dQ/dP)_T$ , we obtain immediately the following,

$$(dH/dP)_T = -SC = -a(T(dV/dT)_P - V), \dots (42)$$

$$(dS/dP)_T = -(dSC/dT)_P = -aT(d^2V/dT^2)_P, \dots (43)$$

$$S_P = + (dQ/dT)_P = - (dQ/dP)_T (dP/dT)_P \\ = + aT (dV/dT)_P (dP/dT)_P, \dots (44)$$

$$S_P - S_V = (SC + aV)(dP/dT)_V = aT(dV/dT)_P(dP/dT)_V, \dots (45)$$

Similarly by substitution from the relation

$$(dV/dT)_P = - (dV/dP)_T (dP/dT)_V,$$

and other relations of the same type, we obtain, in terms of  $V$  and  $T$  as coordinates,

$$(dQ/dV)_T = (dQ/dP)_T (dP/dV)_T = + aT (dP/dT)_V = T(d\Phi/dV)_T, \dots (46)$$

$$(dE/dV)_T = (dQ/dV)_T - aP = aT (dP/dT)_V - aP, \dots (47)$$

$$(dS_V/dV)_T = aT (d^2P/dT^2)_V, \dots (48)$$

$$S_V = (dQ/dT)_V = - (dQ/dV)_T (dV/dT)_V = - aT (dP/dT)_V (dV/dT)_V, \dots (49)$$

Clapeyron's equation may be regarded as a special case of the general relation  $(dQ/dV)_T = aT (dP/dT)_V$ , as applied to a mixture

of the two states of liquid and vapour, since the general relation must hold for any state of the substance. The value of  $(dQ/dV)_T$  for the mixture is evidently the ratio of the latent heat  $L$  to the change of volume  $V - v$  in the vaporisation of unit mass at constant  $T$ . The value of  $(dP/dT)_V$  is the same as the rate of increase of saturation pressure,  $dp/dt$ , so long as both liquid and vapour remain present. We thus obtain

$$L/(V - v) = aT (dp/dt). \dots\dots\dots(50)$$

From the two relations,  $(d\Phi/dV)_T = a (dP/dT)_V$ , and

$$(d\Phi/dP)_T = -a (dV/dT)_P,$$

already given, it is easy to deduce two similar relations,

$$(dT/dV)_\Phi = -a (dP/d\Phi)_V, \dots\dots\dots(51)$$

by substituting  $(d\Phi/dV)_T = - (d\Phi/dT)_V (dT/dV)_\Phi$ ,

$$(dT/dP)_\Phi = a (dV/d\Phi)_P, \dots\dots\dots(52)$$

by substituting  $(d\Phi/dP)_T = - (d\Phi/dT)_P (dT/dP)_\Phi$ .

These four simple and symmetrical relations are often called "The Four Thermodynamical Relations."

It would not be difficult to make out a list of a hundred or more thermodynamical relations between the various coefficients. But there are only two laws of thermodynamics, and only two *independent* thermodynamical relations, namely (24) and (39), or their equivalents, from which all the others are readily deduced by purely formal transformations. In the maze of possible combinations, it is important to keep this fundamental fact in mind.

**Example 27.** Verify the general relation

$$(dV/dT)_P (dP/dT)_\Phi + (dP/dT)_V (dV/dT)_\Phi \\ = (dP/dT)_V (dV/dT)_P. \dots\dots(53)$$

Either side of this equation when multiplied by  $aT$  is an expression for the difference of the specific heats at constant pressure and volume.

Dividing the equation by the right hand side we obtain

$$(dP/dT)_\Phi (dT/dP)_V + (dV/dT)_\Phi (dT/dV)_P = 1. \dots(54)$$

There are several symmetrical relations of this type which may be deduced by suitable permutations of the symbols, but such relations are of little use except as mathematical exercises.\*

**Example 28.** Verify the general relation,

$$(dT/dP)_\Phi - (dT/dP)_H = aV/S. \dots\dots\dots(55)$$

This relation follows by the substitution of

$$aT (dV/dT)_P = S (dT/dP)_P$$

(44), in the expression for  $SC$ . It shows that the cooling-effect in expansion at constant  $H$ , which is denoted by  $C$ , can never exceed the cooling-effect in isentropic expansion, at constant  $\Phi$ , since  $V$  and  $S$  are always positive. The two become nearly equal in the neighbourhood of the critical point when  $V$  is small and  $S$  large, and coincide with  $dp/dt$  at the critical point, where  $S$  is infinite.

*Example 29.* Verify the relation

$$(dH/dT)_P = aT (dV/dT)_P (dP/dT)_P$$

for steam, according to the author's equations, and numerically from Tables IV and V.

The expression for  $H$  gives  $(dH/dT)_P = a(n+1)P(dV/dT)_P$ . The adiabatic equation  $P/T^{n+1} = K$ , gives  $(dP/dT)_P = (n+1)P/T$ . The relation may be verified numerically from the tables at any point by taking  $(dH/dT)_P$  from Table IV, and  $(dV/dT)_P$  from Table V, and multiplying the latter by the factor  $a(n+1)P$ .

*Example 30.* Verify from Tables V and VI the relation

$$-(d\Phi/dP)_T = +a(dV/dT)_P.$$

The mean values of these coefficients taken from 80 to 100 lbs. at 200° C., and from 190° to 210° C. at 90 lbs. respectively are 0.001366 and 0.001362. The mean values will not agree exactly over such a large range of pressure and temperature. The exact value of either at any point is given by the formula  $R/P + auc/T$ , which gives 0.0013618 at 200° C. and 90 lbs.

**189. Direct Deduction from Carnot's Principle.** It is of historical interest to remark that the general expressions for the latent heats of expansion and compression were first given by Clapeyron (*Journal de l'École Polytechnique*, xiv, p. 153, 1834. Translated in Taylor's *Scientific Memoirs*, vol. i, part III, p. 347, 1837) in terms of Carnot's function, and were deduced directly from Carnot's principle before the first law of thermodynamics had been discovered or formulated. The method adopted by Clapeyron was as follows.

According to Carnot, if a quantity of heat  $dQ$  is supplied to any working substance in a heat-engine at a temperature  $t$ , the

quantity of work obtainable in a cycle of range  $dt$  is given by the equation

$$dW = dQ F'(t) dt, \dots \dots \dots (56)$$

where  $F'(t)$  is a function of the temperature only (commonly known as Carnot's function), and is the same for all substances at the same temperature.

The heat supplied per unit mass of any working substance for a small expansion  $dV$  at constant temperature  $t$ , when expressed in terms of the latent heat of expansion, is by definition

$$dQ = (dQ/dV)_T dV. \dots \dots \dots (57)$$

The work done in the cycle is measured on the indicator diagram by the product of the expansion  $dV$  by the mean effective pressure  $(dP/dT)_V dT$ . Hence

$$dW = (dP/dT)_V dT dV. \dots \dots \dots (58)$$

Substituting in Carnot's equation, and dividing by the common factor  $dV dT$ , we obtain the relation

$$(dP/dT)_V = F'(t) (dQ/dV)_T, \dots \dots \dots (59)$$

which takes the form  $(dQ/dV)_T = T (dP/dT)_V$ , if heat is measured in mechanical units and absolute temperature  $T$  is defined as the reciprocal of  $F'(t)$ .

Clapeyron deduced the corresponding expression for  $(dQ/dP)_T$  by the substitution already given. He also obtained another of the most commonly quoted relations in the form of a general expression for  $F'(t)$ , namely,

$$1/F'(t) = (dQ/dV)_P (dT/dP)_V - (dQ/dP)_V (dT/dV)_P, \dots (60)$$

which follows immediately by substituting

$$(dQ/dV)_T = (dQ/dV)_P + (dQ/dP)_V (dP/dV)_T, \dots \dots (61)$$

in the first relation (59).

It would appear that the first two thermodynamical relations might just as well be called Clapeyron's relations, as the general expression for the latent heat of a vapour which he gave at the same time. Carnot had previously employed equivalent methods for calculating the numerical values of his function, but he had not given the corresponding analytical expressions in terms of the partial differential coefficients.

W. Thomson (Lord Kelvin) adopted the first of Clapeyron's relations as the general expression of Carnot's principle in his development of the differential equations of thermodynamics

(*Phil. Mag.*, 1852). He assumed that Carnot's function might be approximately represented by the reciprocal of the temperature measured from the zero of the gas thermometer, but he retained the symbol for Carnot's function in most of the relations for greater generality, because it was at that time uncertain how far the temperature by gas thermometer could be identified with the reciprocal of Carnot's function. Kelvin appears to have been the first to give the general expression (45) for the difference of the specific heats, and to have been the first to show how the variation of specific heat with pressure (48) could be deduced from the consideration that  $dE$  was an exact differential (*Phil. Mag.*, 1852, vol. iv, p. 170). These relations are commonly attributed to Clausius, who gave them some years later in his paper (*Pogg. Ann.*, 125, p. 367, 1865) on the general equations of the mechanical theory of heat, in which he refers to the previous work of Kelvin. The identity of Carnot's function with the reciprocal of  $T$  had by that time been established by the experiments of Joule and Thomson, and the general adoption of Kelvin's absolute scale. Clausius was thereby enabled to give the relations in greater variety in their modern form. But some credit is due to Clapeyron and Kelvin for having been the first to work out the general principles involved in these relations. When once the method has been explained, it is comparatively easy to put the fundamental relations in a variety of different forms by purely mathematical manipulation. It is most important from the experimental standpoint to realise that the multiplication of mathematical transformations cannot lead to any fresh development of physical knowledge, although the choice of suitable expressions may be a matter of convenience in the treatment of any special problem.

**189. Thermodynamical Potential  $G$ .** The potential  $G$  may be defined for the present purpose as the function  $T\Phi - H$ , and its value is readily deduced from those of  $H$  and  $\Phi$ . It provides a convenient method of expression in many cases, and is a useful quantity to tabulate, especially for wet steam, but it cannot give any information which is not otherwise obtainable from  $H$  and  $\Phi$ .

The equation of saturation pressure corresponding to any given assumptions employed in deducing the expressions for  $H$  and  $\Phi$ , is readily found by equating  $G$  for the vapour to  $G$  for the liquid. The simplest type of expression for  $G$  in the case of the liquid is that already given for water.



*Example 31.* Find the expression for  $G$  from Van der Waals' equation, and show that it gives the same equation of saturation pressure as Maxwell's theorem, if  $S_0$  is the same for the liquid and vapour.

Since by the first law,  $dH = Td\Phi + aVdP$ , we have evidently

$$dG = \Phi dT - aVdP. \dots\dots\dots(62)$$

The fundamental relation  $(d\Phi/dP)_T = -a(dV/dT)_P$ , is often deduced from the consideration that  $dG$  is an exact differential, but this is a circular method.

*Example 32.* Verify from the tables that  $(dG/dT)_P = \Phi$ , and  $(dG/dP)_T = -aV$ .

It follows from the expression for  $dG$ , that the thermal equivalent,  $-aVdP$ , of the work done in isothermal flow is equal to the decrease of  $G$ . Similarly the work done in adiabatic flow is equivalent to the increase of  $G$  diminished by  $\Phi$  times the increase of  $T$ , or to  $\Phi$  times the drop of temperature minus the drop of  $G$ . These expressions are often useful, especially in finding the adiabatic drop of  $H$  for wet steam.

From the expression assumed for  $G$  in the case of the liquid under saturation pressure, we have the following simple relations

$$(dG/dT)_s = s \log_e (T/T_0) - 0.003/T_0, \dots\dots\dots(63)$$

$$T(dG/dT)_s - G_s = st - 0.003, \dots\dots\dots(64)$$

in which the small constants are practically negligible. These are useful in considering the flow of wet steam.

By equating the values of  $dG/dT$  for the liquid and vapour at saturation we obtain Clapeyron's equation in the form

$$\Phi - \phi = a(V - v)(dp/dt) = L/T. \dots\dots\dots(65)$$

The foregoing summary, together with the examples and equations given in the body of the work, sufficiently illustrates the application of the laws of thermodynamics to the properties of a simple fluid such as steam. There are many other thermodynamical relations which may be required in other branches of physics, but the general principles remain the same, so that when the application to a simple case has once been mastered, the student should have less difficulty in following the development of more complicated relations. An index of coefficients, alphabetically arranged, is given at the end of Appendix III, pp. 521-526.

## APPENDIX II

### ON THE USE OF THE DIAGRAM.

**190. On the Choice of a Diagram.** Many problems connected with the properties of steam can be readily solved by graphic methods with a degree of approximation sufficient for practical purposes. The kind of diagram best suited for any particular purpose naturally depends to some extent on the nature of the problem to be solved, but for general use it is desirable to employ a single diagram on which all the required properties may be adequately represented in a manner suitable for exact measurement. The diagram issued in connection with this book has been selected with the special object of illustrating the properties of steam, and facilitating the measurements required in practical calculations. It will be well, however, to consider briefly some of the other diagrams commonly employed, in order to explain more clearly the requirements to be satisfied and the conditions on which the choice depends.

*The Indicator or PV Diagram* is primarily required for measuring the work done in the cylinder of a reciprocating engine, for which purpose it is the only method available. It is also appropriate for exhibiting the results of experiment over a limited range when the observed quantities are the pressure and volume, and has been employed most frequently in theoretical works as a graphic method of illustrating the principles of thermodynamics. Work, heat, and energy, are naturally represented by areas, which are troublesome to measure, but otherwise afford the most appropriate representation. The state of the substance with regard to temperature and entropy may be represented by drawing families of isothermal and adiabatic curves. These curves are instructive in relation to the actual expansion curves obtained by the use of the indicator, but are difficult to construct accurately, and intersect at inconveniently sharp angles, even in the best part of the diagram. The indicator diagram is essential to the scientific study of the steam-engine, but is in many ways most unsuitable for the representation of the properties of the working substance. Except for a limited range,

if any two coordinates are given defining the state, and the object is to determine with a fair degree of accuracy the numerical values of the remaining quantities, the indicator diagram is one of the most inappropriate that could possibly be devised. The uniform scales of pressure and volume, which are essential for the measurement of work in terms of area, involve excessive inequality of scale for all the other properties required, and preclude the attainment of uniform *proportionate accuracy*—the chief desideratum in experimental measurement—even in the case of pressure and volume. The isothermals and adiabatics become inextricably confused at high pressures and large volumes, and it is practically impossible to distinguish the lines of constant total heat from the isothermals in the dry region. The difficulty of scale is avoided in the practical use of the indicator by using many different springs with different scales, but such a procedure would evidently be impracticable in using the diagram for representing the properties of steam over an extended range.

The *Temperature Entropy, or  $T\Phi$ , Diagram* is also most instructive for theoretical purposes, but probably owes much of its popularity in practice to its great superiority over the indicator diagram in point of suitability of scale over an extended range for most of the quantities required. The areas representing quantities of heat are of a convenient shape, and the drop of total heat, required in so many problems, is often estimated by measuring the appropriate area on the diagram. The inconvenience of having to measure areas is commonly avoided by drawing lines of constant  $H$  on the diagram. This is easily done in the wet region, but the lines are peculiar in shape, and change their direction abruptly in crossing the border curve. The same is true of the lines of constant pressure and volume, which intersect at sharp angles and are difficult to distinguish in the dry region. There is no simple scale for either pressure or volume, so that, although the small volumes and the low pressures are not so crowded as in the  $PV$  diagram, it is difficult to read either accurately owing to the variability of scale in different parts of the diagram. The only uniform scales are those of temperature and entropy, but the numerical value of the latter is rarely required. The chief advantage of the diagram is the ease of following adiabatic expansion, since the lines of constant entropy are straight.

*The Mollier Diagram.* A great practical improvement is effected by taking  $H$  as the ordinate in place of  $T$ , which makes it

possible to measure the adiabatic heat-drop in the simplest way on a scale of equal parts. An additional advantage is that the lines of constant pressure cross the saturation line without any abrupt change of direction, in virtue of the fundamental relation  $dH/d\Phi = T$  at constant pressure. But the scale of pressure varies considerably from one end of the diagram to the other, which makes it necessary to rule the lines somewhat closely, and precludes accuracy of measurement in locating the state-point unless the pressure is a round number. The chief defect of the  $H\Phi$  diagram is that the lines of constant volume (the other quantity most often required) cannot be inserted without risk of confusion with the lines of constant pressure. For this reason, a separate diagram is often employed for the volume. Mollier takes  $H$  and  $P$  as coordinates for this purpose, but the adoption of a scale of equal parts for the pressure involves the consequence that the scales of volume, temperature, and dryness, are so minute in the region of low pressures that the diagram is useless where it is most required.

*The  $H \log P$  Diagram.* In the diagram issued with the Steam Tables the logarithm of the pressure is taken as abscissa with  $H$  as ordinate. This has the advantage that equal ratios of expansion, which are of equal importance in practice, are represented by equal intervals. It also gives a more open scale for the pressure than the Mollier diagram, and makes it possible to read the values on a simple logarithmic scale with uniform proportionate accuracy in all parts of the diagram. The lines of constant volume are readily shown on the same diagram, and the volumes can be read on the same logarithmic scale with almost equal ease. The adiabatics are no longer straight, but their curvature is slight, and they cross the saturation line without any abrupt change of direction, in virtue of the fundamental relation  $dH/dP = \alpha V$  at constant  $\Phi$ . It is almost as easy to follow adiabatic expansion as in the entropy diagram. The essential point, however, is that all the required quantities are accurately measurable on scales which do not vary materially in different parts of the diagram.

**191. Description of the Diagram.** The scale of pressure employed is the familiar logarithmic scale of the 25 cm. slide-rule, which every student possesses, in which the ratio 100/1 is represented by 25 cms., and other ratios in proportion to their logarithms. The lines of constant pressure, the fundamental co-ordinate in the case of the steam-engine, are vertical straight lines,

of which very few need be drawn, since the pressures are read off with the slide-rule scale as easily as with a scale of equal parts, but with the additional advantage of uniform *proportionate* accuracy.

The lines of constant volume are slightly curved and inclined to the vertical, but the scale of volumes is so nearly the same as that of pressures in all parts of the diagram that the volumes can be read on the same logarithmic scale with nearly equal ease.

The saturation line, dividing the wet from the dry region, is nearly straight, and but slightly inclined to the horizontal.

The adiabatics, or lines of constant entropy, are diagonal curves (dotted) of nearly equal curvature and spacing, and are inclined at a favourable angle to the lines of constant pressure, temperature, volume, and total heat. In virtue of the fundamental relation  $(dH/dP) = aV$  at constant entropy, the adiabatics cross the saturation line without any abrupt change of direction, since the change of volume is contiguous. By using a set-square with a curved diagonal, as described below, it is almost as easy to follow adiabatic expansion as in the entropy diagram, but the new diagram has the advantage that the initial and final pressures can be more accurately located.

The lines of constant dryness are easily drawn in the wet region, but a few only are inserted, because they are very seldom required when the volume and all the other quantities are shown on one diagram.

Lines of constant temperature are vertical straight lines in the wet region, but are not drawn, because it is easy to read the temperature, if required, from the scale of saturation temperature and pressure at the base of the diagram.

It should be observed that the horizontal lines of constant total heat and the vertical lines of constant pressure, are not closely ruled (as is customary) throughout the whole length and breadth of the diagram, but a few only are inserted as reference lines. The reason of this is that it is more expeditious and accurate in practice to read the values from the nearest reference line with a millimetre or logarithmic scale placed on the diagram than to refer continually to finely divided scales at the side. The constant volume lines are ruled about twice as closely as the pressure lines, because the scale of volumes is not so accurately logarithmic. The temperature lines are ruled for each  $20^\circ$  in the dry region, to facilitate the use of a millimetre scale for interpolation, as the scale is very nearly  $2^\circ$  per mm. The entropy scale is  $T$  mms. per unit

along a vertical in any part of the diagram, and is uniform along each vertical in the wet region.

*Auxiliary Curves.* A curve of Latent Heat,  $L$ , is drawn in the wet region, from which the values of the latent heat at any pressure may be read on the total heat scale. This curve is useful in solving problems involving latent heat without reference to the tables. The heat of the liquid  $h$ , if required, may be found very accurately by adding to  $t$  the ordinate of the water-heat curve, given in the lower right-hand corner of the diagram. The curve of the thermodynamic potential of water  $G = T\phi - h$ , shown in the same region of the diagram, affords the most expeditious method of calculating the total heat of wet steam in any state by the formula  $H = T\Phi - G$ , when the temperature and entropy are given.

**192. Method of Using the Diagram with Divided Set-Square.** Values sufficiently close for many purposes may be obtained by simple inspection, but in order to obtain accurate results from the diagram, it is most convenient to fix it on a drawing-board, adjusting it carefully so that the straight edge of the T-square is parallel to the horizontal lines of constant total heat. The T-square may be used to refer the reading of total heat at any point to a scale at the side, and a set-square may be employed to give the corresponding value of the pressure by the scale at the top. Or the distances on the diagram may be measured with a pair of dividers from the nearest reference lines, and read off on the millimetre and logarithmic scales of an ordinary 25 cm. slide-rule. But a more accurate and expeditious method is to employ a special set-square of transparent material, with a millimetre scale divided on its under side along the vertical edge, and a log. scale similarly divided along the horizontal edge. The millimetre scale serves for temperature and total heat, and the log. scale for pressure and volume. The diagonal edge of the set-square is curved to fit the mean adiabatic, and is useful for following adiabatic expansion or finding the entropy.

*To read the Entropy.* The only scale that is materially variable in different parts of the diagram is that of entropy. In order to meet this, without confusing the diagram by drawing too many lines, the isentropics or adiabatics are drawn only for each tenth of a unit of entropy from 1.4 to 2.1, and the scale of entropy is divided to hundredths along each of the vertical reference line of the pressure scale. To find the numerical value of the entropy

corresponding to any given point on the diagram, mark the required point with a fine pencil, find the part of the curved edge of the set-square (or of a paper template traced and cut to fit the mean adiabatic 1.7) which corresponds most nearly in curvature with the nearest adiabatic, set the curve to pass through the pencil dot and divide the entropy scales equally on either side. By estimating tenths of a division, the required value of the entropy can be found to 1, in the third place of decimals.

*To read the Total Heat at any Point.* Read the vertical distance in mms. and tenths above the nearest reference line, and add the reading to the value marked on the reference line.

*To measure the Heat-Drop between two given Points.* Adjust the T-square to pass through the lower point, and slide the set-square until its vertical edge meets the upper point. The drop is given by the vertical scale reading in mms.; but unless the T-square and drawing board are very perfect, it is usually better to measure each value of  $H$  from the nearest reference line, and take the difference.

*To read the Pressure at any Point on the Diagram.* Place the set-square on the diagram, with its vertical edge to the right, and the log. scale reading backwards from right to left, the divisions being on the under side. Slide the set-square along the T-square until its vertical edge passes through the required point. The pressure is then read on the log. scale at the point where it is crossed by the 1, 10, or 100 lb. reference lines of pressure. Thus if the pressure is 157 lbs., the 100 line will cross the scale at 1.57, or the 10 line at 15.7. Similarly, to mark a vertical line on the diagram for any given pressure, say 157 lbs., slide the set-square horizontally along the T-square to the right till the division 1.57 of the log. scale meets the edge of the 100 lb. line, and rule a short vertical line with a fine pencil along the vertical edge of the set-square near the required temperature or entropy. Since it is generally necessary to mark the pressure in this way with a short vertical line, it is most convenient to have the log. scale reading backwards from right to left, which also suits best for reading volumes.

*To read the Volume.* Lay the log. scale across the lines of constant volume so that the numbers correspond. Thus, if the volume is between 50 and 70, set the divisions 50 and 70, or 5 and 7, on the log. scale to fit as nearly as possible with the 50 and 70 lines of constant volume. The fit can usually be made exact by sloping the scale. If not, adjust the errors at either end of the 50 to 70

interval by estimation in the same proportion as the whole interval is divided by the required point. Read the required point on the scale, estimating tenths of a division as usual.

*To read the Temperature for Superheated Steam.* Place the mm. scale across the lines of constant temperature so that the cm. divisions nearly fit. Adjust the small errors at either end, if any, proportionately to the division of the interval by the required point. Read the point in mms. and tenths. Multiply by 2, and add the result to the temperature marked on the lower line.

*To mark the State-point, given  $P$  and  $T$  for Superheated Steam.* Set the vertical edge of the set-square for the required pressure, slide the square vertically till the cm. divisions fit the lines of constant temperature near the required point, mark the required temperature with a fine pencil dot by the aid of the mm. scale.

*To mark the Final State-Point, given  $P$  and  $\Phi$ .* Rule a short vertical for the final  $P$  to cross the adiabetic. Adjust the curved edge of the set-square to the value of  $\Phi$  as previously explained, and mark the required point with a dot, or by ruling a short piece of the adiabetic. Or conversely, rule a short piece of the adiabetic, and mark the required pressure on it.

*To find  $P$  and  $H$ , when  $V$  and  $\Phi$  are given.* Rule a short piece of the adiabetic, adjust the log. scale to fit the lines of constant volume, and cross the adiabetic at the given value of  $V$ . Hold a pencil or a divider point at the crossing while shifting the set-square so that its vertical edge rests against the point and its horizontal edge fits the nearest reference line of  $H$ . Read the vertical scale for  $H$  at the point, and the log. scale for  $P$  where it crosses the 1, 10, or 100 line.

*To read the Temperature for Saturated Steam at any Pressure.* Reverse the log. scale to read from left to right, and lay it along the temperature scale at the base of the diagram. To find  $h$  for the liquid, add the ordinate of the  $h - t$  curve to the value of  $t$ .

**193. Find the Heat-Drop in Adiabatic Expansion.** The commonest use of the diagram is to find the values of any one of the properties  $P$ ,  $T$ ,  $H$ ,  $V$ , or  $\Phi$ , when any other two are given defining the state. The solution of almost any problem may be worked out in this way to a fair degree of approximation without using the tables, by reading the required values at suitably selected points according to the data and conditions assumed in the problem.

One of the most familiar examples is to find the efficiency of the



Rankine cycle, or the heat-drop in adiabatic expansion, which will be considered in detail as affording a good illustration of the use of the diagram in following adiabatic expansion. Since the adiabatic heat-drop depends only on the properties of the working substance, the result can be worked out theoretically to a high order of accuracy from the tables or equations; the accuracy obtainable with the diagram is necessarily limited, but is greater than might at first sight be supposed, on account of the use of the logarithmic scale for the pressure and volume. For instance, in the following example, the initial value of  $H$  can be found to the limit of accuracy of reading the millimetre scale for  $H$ , since the data for  $P$  and  $T$  are given. The error should not exceed a fifth of a mm. or 0.2 cal. For the final state the pressure is only 1.76 lbs., and it might be thought that the decimals could be neglected, since the initial pressure cannot be read closer than about half a lb. But an error of a hundredth of a lb. in the final pressure is as important as an error of half a lb. in the initial pressure. Both correspond nearly in fact to an error of a fifth of a calorie in the heat-drop, as is easily estimated from the fundamental relation  $(dH/dP)_\phi = aV$ , which gives 0.17 cal. for the error in  $H$  due to an error 0.01 lb. in  $P$ , under the condition  $\Phi$  constant. The advantage of the log. scale of pressure is that it is just as easy to read to 0.01 lb. at the final pressure as to 1 lb. at the initial pressure. The resulting error in the measurement of the heat-drop (182.5 cal. in the present example) is seen to be of the order of 1 in 1000 only for an error 1 in 176 in the final pressure. In general the results obtainable by the use of the log. scale are much more accurate than might appear to be the case at first sight. But it will readily be understood that this order of accuracy could not be attained without the use of finely divided scales, rendered possible by a proper choice of coordinates for the diagram.

*Example.* Find the heat-drop in adiabatic expansion, and the efficiency of the Rankine cycle, for the following experimental data.

Initial temperature, 288° C., pressure, 142.5 lbs. (gauge), vacuum, 25.9 inches, barometer, 29.5 inches (14.5 lbs.). Whence  $P' = 157$  lbs. abs.,  $P'' = 1.76$  lbs. abs.

*To locate the Initial State-point.* Lay the set-square ABC on the diagram, as shown in the annexed figure on a reduced scale, so that the division 1.57 of the log. scale lies on the 100 lb. reference line. The vertical edge then corresponds to 157 lbs. Mark a fine pencil dot on this vertical for  $t$  at 1.5 mms. above the 280° line

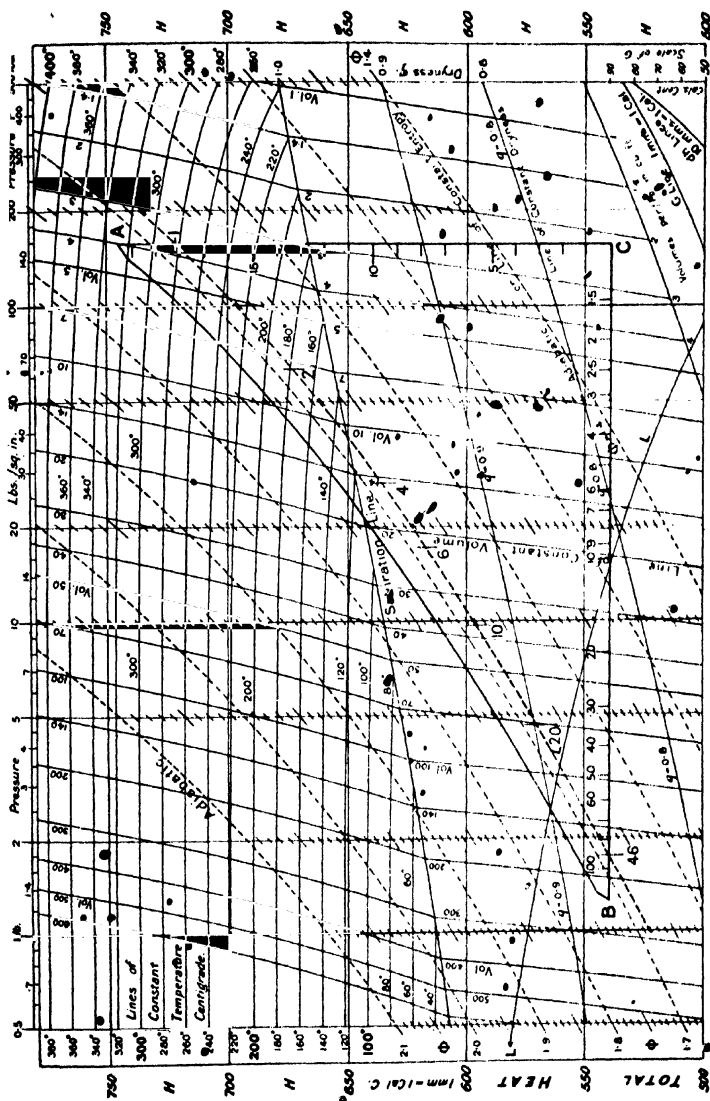


Fig. 36. Use of the Divided Set-Square with the  $H \log P$  diagram.

of constant  $t$ , which gives the initial state-point, (1) at  $233^{\circ}\text{C}$ . This point is found to be 21.8 mms. above the 700 reference line of  $H$ , whence  $H' = 721.8$ .

Read  $\Phi'$  with the curved edge of the set-square, whence  $\Phi' = 1.682$ .

Read  $V'$  on the log. scale between divisions 3 and 4, whence  $V' = 8.69$ .

*To locate the Final State-point.* Set the square so that the division 1.76 of the log. scale lies on the 1 lb. reference line. Rule a short line along the vertical edge at  $P = 1.76$  to cross the adiabatic  $\Phi = 1.682$ . Mark the exact point of crossing by ruling a short piece of the adiabatic with the curved edge. This gives the final state-point, 46, in the figure. The required heat-drop can be read off directly on the vertical scale by setting the T-square to pass through the final state-point and sliding the set-square into the position ABC in the figure, to meet the initial state-point. But a more accurate result may be obtained by measuring  $H''$  from the 500 reference line, which gives  $H'' = 539.3$ . Read  $V'' = 169$  (expansion ratio 46) on the log. scale, and  $t'' = h'' = 49.6$ , on the scale at the base.

The required heat-drop is,  $H' - H'' = 721.8 - 539.3 = 182.5$ .

The work done by the feed-pump is  $a(P' - P'')v'' = 0.26$ .

The heat supplied is,  $H' - h'' = 721.8 - 49.6 = 672.2$ .

The efficiency of the Rankine cycle is  $182.2/672.2 = .2710$ .

The velocity due to reversible adiabatic expansion is found from the heat-drop by the formula,  $U = 300.2\sqrt{(H' - H'')}$ , which gives  $U = 4055$  ft./sec. A velocity scale is often given on the diagram, but the scale is no use for *changes* of velocity, and it is usually best to work the result on the slide-rule.

The initial and final volumes are not required in the above example, but are useful for other purposes, e.g. in the case of incomplete expansion, or for finding the appropriate dimensions of a cylinder or turbine, or the final section of a nozzle.

**194. Incomplete Expansion.** The expansion in the ideal Rankine cycle is supposed to be continued down to the condenser pressure. In practice this would require cylinders of an excessive size, and would give very low mechanical efficiency. It is therefore of interest to investigate the necessary loss of efficiency due to incomplete expansion, and to compare it with the actual gain of mechanical efficiency. There are other sources of loss in practice, such as leakage and cylinder condensation, but the loss due to

incomplete expansion can be separately investigated, and affords a good illustration of the use of the  $H \log P$  diagram, because such problems are difficult to solve with the tables, or the Mollier diagram. In order to find the thermal equivalent  $AW$  of the work done by the steam in the cylinder, when the expansion ratio is given, and the steam is released at the end of the stroke at a pressure  $P''$  greater than the condenser pressure  $P_0$ , we have simply to add to the heat-drop  $H' - H''$  in adiabatic expansion from  $P'$  to  $P''$ , the thermal equivalent  $aV''(P'' - P_0)$ , of the work due to the excess of the release pressure over the back-pressure, thus,

$$AW = H' - H'' + aV''(P'' - P_0).$$

The heat-drop  $H' - H''$  for a given expansion ratio  $V''/V'$ , and the release pressure  $P''$ , are easily found by observing the intersection of the adiabatic with the volume line  $V''$ , but it is essential for this purpose that volume and entropy should be shown on the same diagram as the pressure and total heat.

Taking steam in the initial state given in the preceding example, namely,  $\Phi' = 1.682$ ,  $V' = 3.69$  and referring to the same Fig. 36, the pressures corresponding to 2, 4, 6, 10, and 20 expansions are marked by short vertical lines on the adiabatic  $\Phi = 1.682$ . The values of the pressure  $P''$  and total heat  $H''$  are read off as already explained, and the remainder of the calculation proceeds very simply as indicated in the following table. The first line gives the expansion ratio, or the reciprocal of the cut-off. The second line gives the volume at release. The third line gives the pressure at release, and the fourth the total heat. Adding the product  $aV''(P'' - P_0)$  to the heat-drop  $H' - H''$  we obtain the thermal equivalent  $AW$  of the maximum work indicated, or obtainable in the cylinder per lb. of steam, given in line 7. The quotient  $1414/AW$  gives the theoretical minimum consumption in lbs. per I.H.P.-hour, line 8, which reaches the limit 7.8 for the ideal Rankine cycle when the expansion is complete, but does not at all represent the efficiencies obtainable in practice, when the power is regulated by varying the expansion ratio.

Some idea of the necessity of incomplete expansion (even if clearance and other losses are neglected) is given by working out the brake efficiencies for a single cylinder of given volume. The volume is taken as 8.69 cubic feet, requiring 1 lb. of steam per cycle, under the initial conditions when the expansion ratio is unity. The equivalent  $AW$  of the indicated work per cycle is then

Table showing effect of incomplete expansion.

Initial state,  $t' = 283^\circ$ ,  $P' = 157$  lbs.,  $V' = 3.69$  ft.<sup>3</sup>,  $H' = 721.8$ ,  $\Phi' = 1.682$ .

Condenser pressure,  $P_0 = 1.76$ , cylinder volume taken as 8.00 cubic feet.

Expansions	1	2	4	6	10	20	40.3
Final state $\begin{cases} V'' \\ P'' \\ H'' \end{cases}$	$\begin{cases} 3.69 \\ 157 \\ 721.8 \end{cases}$	$\begin{cases} 7.38 \\ 63.9 \\ 673.4 \end{cases}$	$\begin{cases} 14.76 \\ 27.3 \\ 636.2 \end{cases}$	$\begin{cases} 22.14 \\ 17.2 \\ 617.8 \end{cases}$	$\begin{cases} 36.9 \\ 9.76 \\ 590.0 \end{cases}$	$\begin{cases} 73.8 \\ 4.66 \\ 568.5 \end{cases}$	$\begin{cases} 169 \\ 1.76 \\ 539.3 \end{cases}$
$H' - H''$	0	48.4	85.6	104.0	125.8	153.3	182.5
$aV''(P'' - P_0)$	58.4	46.6	38.4	34.9	30.1	21.8	0
I. $\Delta W$ /lb.	58.4	95.0	124.0	138.9	155.9	175.1	182.5
Lbs./I.H.P.H.	24.2	14.9	11.4	10.2	9.1	8.1	7.8
Actual lbs./I.H.P.H.	26.6	17.9	16.0	16.3	18.2	24.3	44.0
I. $\Delta W$ /cycle	58.4	47.5	31.0	23.2	15.59	8.76	3.94
Brake $\Delta W$ /lb.	54	86	106	111	109.5	82.5	Neg.
Lbs./B.H.P.H.	26.2	16.5	13.4	12.7	12.9	17.2	Inf.
Actual lbs./B.H.P.H.	28.8	19.8	18.8	20.3	25.2	51.6	"

found by dividing the indicated  $\Delta W$  per lb. by the expansion ratio. The figures for the I.  $\Delta W$  per cycle are proportional to the I.H.P. at a given speed. The mechanical losses per cycle may be taken as being independent of the load, and as equivalent to 4.6 cal., which gives a mechanical efficiency of 80 per cent. at 6 expansions. Deducting this constant loss from the values of the indicated  $\Delta W$  per cycle, and dividing by the lbs. per cycle in each case, we obtain the figures given in the next line for the equivalent of the work done on the brake per lb. of steam. This reaches a maximum at about 7 expansions, but becomes *negative* before the expansion is complete. The figures given for the consumption in lbs. of steam per brake horse-power-hour, are much better than those attainable in practice with a single cylinder, owing to the neglect of other losses, but suffice to show the necessity of incomplete expansion in practice. The *indicated* efficiency would vary with expansion ratio in a similar manner to the brake efficiency for a single cylinder, if account were taken of losses due to leakage and condensation, as indicated by the values given in the line representing "actual" lbs./I.H.P.H., calculated by the method explained below, in the section on condensation and leakage.

**195. Regulation by Throttling.** Another common method of regulation is by simple throttling, with a fixed boiler pressure and

expansion-ratio. In this case the initial value of the total heat  $H'$  remains constant while the initial pressure is varied. For any given value of  $P'$ , the initial volume  $V'$  is read off on the line  $H'$ , or calculated, if the steam is dry, by the equation for  $V$  in terms of  $H$  and  $P$ . The final volume  $V''$  is found by multiplying  $V'$  by the given expansion-ratio. The final pressure  $P''$  is obtained on the diagram from the intersection of the adiabatic through  $H'P'$  with the volume line  $V''$ .

The equivalent  $AW$  of the indicated work per lb. is given by the same formula as in the previous example. When  $H'$  and  $V''/V'$  are given, it will be found that the heat-drop  $H' - H''$  is nearly independent of  $P'$ . The variations of  $H' - H''$  in the following example are so small that it might have been taken as constant and equal to 88 cal.

Table showing effect of regulation by throttling.

Initial state  $H' = 700$ . Expansion ratio  $V''/V' = 5$ .

Cylinder volume taken as 3.69 cubic feet. Condenser pressure, 2 lbs./sq. in.

Initial state $\left\{ \begin{array}{l} P' \\ V' \end{array} \right.$	500	300	200	150	100	50	20
	1.070	1.78	2.66	3.54	5.30	10.60	26.5
Final state $\left\{ \begin{array}{l} V'' \\ P'' \end{array} \right.$	5.35	8.90	13.3	17.7	26.5	53.0	132.5
	74.0	43.7	28.9	21.4	14.1	6.8	2.62
$aV''(P'' - P_0)$	39.6	38.2	36.7	35.3	32.9	26.3	8.5
$H' - H''$	88.8	88.2	88.0	87.9	87.8	88.0	88.7
I.A.W./lb.	128.4	126.4	124.9	123.2	120.7	114.3	97.2
Lbs./I.H.P.H.	11.0	11.2	11.3	11.5	11.7	12.4	14.6
I.A.W./cycle	88.3	52.2	34.6	25.7	16.9	7.9	2.7
B.A.W./cycle	83.7	47.6	30.0	21.1	12.3	3.3	(-)
B.A.W./lb.	121	115	108	101	88.2	47.4	(0)
Lbs./B.H.P.H.	11.7	12.3	13.1	14.0	15.0	30.0	Inf.
Actual lbs./B.H.P.H.	17.3	18.3	19.4	20.7	23.6	44.5	„

It will be seen that there is little loss of indicated efficiency by throttling over a wide range of power. In practice, the variation would generally be less owing to increase of condensation and leakage with increase of pressure. The throttling method has the advantage over the variable expansion method that these losses are reduced at low loads. On the other hand, if the expansion ratio is fixed to give a fair degree of efficiency at normal loads, the engine will not take a large overload without a corresponding increase of boiler pressure.

**196. Effect of Condensation and Leakage.** Losses due to clearance, condensation, and leakage, depend rather on the type and arrangement of the engine than on the properties of the working fluid. For a given engine, working under given conditions of initial and final pressure and temperature, these losses may often be represented roughly by adding a constant quantity to the consumption per hour. For a given speed, the "missing quantity"  $M_q$ , measured in lb./cycle, would also be constant. The "actual" consumption per cycle, or "cylinder feed," would be  $M_q + V_c/V''$ , in place of  $V_c/V''$ , where  $V_c$  is the cylinder volume, and  $V''$  the volume per lb. at release. The "actual" consumption per I.H.P.H. or per B.H.P.H., can be estimated on this basis by multiplying the theoretical consumption already given by the factor  $(1 + M_q V''/V_c)$ . With suitable values of  $M_q$ , this method gives figures for the consumption more nearly resembling those attainable in practice. But it is better to reverse the procedure, and to calculate the values of  $M_q$  for different engines by comparing the theoretical with the observed performance. The study of these losses affords a very instructive exercise on the theory of the steam-engine, but is so varied in detail for different types of engine that it would be impossible to discuss it intelligibly in the present work as an illustration of the use of the diagram. The figures given in the above tables for the "actual" consumption in a single cylinder engine should be regarded merely as an illustration of the effect of assuming (1) a constant value 0.10 lb. for  $M_q$  in the case of variable expansion, and (2) a value  $P'/1500$ , proportional to  $P'$ , in the throttling table, where the initial pressure is variable. For a detailed discussion of experimental and theoretical methods of estimating  $M_q$ , the student may refer to the paper previously cited "On the Law of Condensation of Steam" (*Proc. Inst. C. E.*, 1898). A general account of the theory is also given in many textbooks, e.g. Dalby, *Steam-Power*, p. 232.

Losses due to condensation and leakage cannot easily be represented on a diagram. The method is most appropriate for representing continuous expansion, with or without friction, as in a turbine or nozzle, by curves drawn on the diagram as in Figs. 28 and 32. The single copy of the diagram supplied with these Tables would be inadequate for long-continued use, and its accuracy is somewhat impaired by folding. Arrangements have accordingly been made by the Publishers for supplying additional copies of the diagram at a moderate price.

Special scales for reading the diagram have been constructed. A set-square with finely divided scales in transparent celluloid may be obtained from Mr W. H. Harling, 17, Finsbury Pavement, London, E.C., price 5s., and a short millimetre and logarithmic scale in celluloid, price 1s. Prints of the set-square and scale, on paper similar to the diagram, may be had from Mr Harling for temporary use or Examination purposes.

The steam tables contained in the following Appendix III are published separately, including an explanation of the diagram.



## APPENDIX III

### STEAM TABLES

**197. Units and Constants.** *Systems of Units.* Values are tabulated on the following three systems:

F.P.C., or Foot-Pound-Centigrade, with pressure in pounds per square inch, volume in cubic feet per pound, and temperature on the Centigrade scale.

F.P.F., or Foot-Pound-Fahrenheit, with the same units of pressure and volume, but with temperature on the Fahrenheit scale.

K.M.C., or Kilogram-Metre-Centigrade, with pressure in kilos per sq. cm., volume in cubic metres per kilo, and temperature on the Centigrade scale.

*Reduction Factors.* The following reduction factors are assumed for metric units:

One Foot = 0.304800 Metre. One Pound = 0.453592 Kilogram, which give the following factors for the derived units:

Density: 1 pound per cubic foot = 16.0184 kilograms per cubic metre.

Pressure: 1 pound per square inch = 0.070307 kilo per square centimetre.

Work: 1 Foot-Pound = 0.138255 Kilogram-Metre.

*The Intensity of Gravity* in London at sea-level is taken as the standard for the tables, and is assumed to be 1 in 2000 greater than the conventional value of the mean intensity in latitude 45°, namely 980.665 C.G.S., which gives

$$g = 9.8116 \text{ metres/sec.}^2 \text{ or } 32.190 \text{ ft./sec.}^2 \text{ at London.}$$

*The Boiling-Point of Water*, 100° C. or 212° F., is defined as the temperature of steam condensing under a pressure of one standard atmosphere, equivalent to 760 mm. of mercury at 0° C. at a place where  $g = 980.665$  C.G.S.

1 atmo. = 14.6960 pounds per sq. in., or 1.08274 kilos per sq. cm. (London).

*Units of Heat.* The unit of heat on the F.P.C. system, with the pound as unit of mass, is the Pound-Calorie; on the K.M.C.

system, the Kilo-Caloric. But the numbers representing Total Heat, etc., in pound-calories per pound are the same as those representing the same quantities in kilo-calories per kilogram. The total heat of water at 100° C. may be stated as 100 mean calories centigrade on either system, reckoned from 0° C.

The *Mean Thermal Unit* is adopted in these tables as the unit of heat. The mean thermal unit on the centigrade scale is 1/100th part of the change of total heat of unit mass of water under saturation pressure from 0° C. to 100° C. Similarly the unit of heat on the F.P.F. system is taken as the Mean British Thermal Unit, or B.Th.U., which is 1/180th part of the quantity of heat required to raise 1 lb. of water from 32° F. to 212° F.

*Fundamental Constants for Water and Steam.* The following values, expressed in terms of the mean specific heat of water between the freezing- and boiling-points taken as unity, are the same in all three systems of units:

Minimum specific heat of water,  $s = 0.99696$ .

Gas constant for steam per unit mass,  $R = 0.11012$ .

Specific heat of steam at zero pressure,  $S_0 = 0.47719$ .

Ratio,  $S_0/R = n + 1 = 13/3$ . Index,  $n = 10/3$ .

The following fundamental constants depend on the temperature scale:

Latent heat of steam at B.P.,  $L = 539.30$  C. = 970.74 F.

Absolute temperature,  $T = t + 273.10$  C. =  $t + 459.58$  F.

*Values of the Mechanical Equivalent.* The absolute value of the mean gram-caloric C. is taken as 4.1868 joules, or  $4.1868 \times 10^7$  C.G.S., from the results of experiments on the total heat  $h$  of water by the continuous electric and continuous mixture methods (*Phil. Trans.*, A, 199, pp. 57-148, 1902; A, 212, pp. 1-32, 1912).

The corresponding values of the equivalent  $J$  of the mean thermal unit in gravitational units of work for gravity at London are as follows:

$$J = 1400.00 \text{ (F.P.C.)}, \quad J = 777.8 \text{ (F.P.F.)}, \quad J = 426.7 \text{ (K.M.C.)},$$

which must be increased by 1 in 2000 for gravity in latitude 45°.

The reciprocal of  $J$  is denoted by  $A$ . The factor for reducing a product of dimensions  $PV$  to thermal units is denoted by  $a$ , and has the following values:

$$a = 144/1400 \text{ (F.P.C.)}, \quad a = 144/777.8 \text{ (F.P.F.)},$$

$$a = 10000/426.7 \text{ (K.M.C.)}.$$

**198. Summary of Equations.** *Expression for the Total Heat of Water  $h$ .* The effect of the ice molecules on the total heat near the freezing-point may be neglected in steam-engine work. The effect of the steam molecules in the liquid is most simply represented for water under saturation pressure by the equation

$$h = st + vL/(V_s - v) - 0.008 = st + (H_s - st)v/V_s - 0.008 = H_s - L$$

where  $v$  and  $V_s$  are the volumes of water and dry saturated steam at  $t$ ,  $H_s$  and  $L$  the total and latent heats.

The entropy of water under saturation pressure,

$$\phi = s \log_e (T/T_0) + vL/T (V_s - v) - 0.000010.$$

*Expression for the Total Heat of Steam  $H$ .* The general expression, deduced from experiments on the specific heat  $S$  and the Joule-Thomson "cooling-effect,"  $C = (dT/dP)_H$  for dry steam in any state, is as follows:

$$H = S_0 T - SCP + B,$$

where  $S = S_0 + an(n+1)cP/T$ , and  $SC = a(n+1)c - ab$ .

$B$  is a constant deduced from  $L = 539.30$  at  $100^\circ \text{C.}$ , giving  $B = 464.00$  cals. C., or  $835.20$  B.Th.U./lb. F.

*Characteristic Equation for Dry Steam giving  $V$  in terms of  $P$  and  $T$ .*  $V - b = RT/aP - c$ , where  $c = c_1 (T_1/T)^{10/3}$ .

$R/a = 1.07061$ ,  $T_1 = 373.10^\circ$ ,  $c_1 = 0.4213$ ,  $b = 0.01602$  (F.P.C.),  
 $R/a = 0.59479$ ,  $T_1 = 671.58^\circ$ ,  $c_1 = 0.4213$ ,  $b = 0.01602$  (F.P.F.),  
 $R/a = 0.004699$ ,  $T_1 = 373.10^\circ$ ,  $c_1 = 0.02630$ ,  $b = 0.00100$  (K.M.C.).

The "co-volume"  $b$  is taken as the volume of unit mass of water at  $0^\circ \text{C.}$ , or  $32^\circ \text{F.}$

The "co-aggregation volume"  $c$  is deduced from the cooling-effect  $C$ , and expresses the diminution of volume from the ideal value  $RT/aP$  due to co-aggregation or pairing of molecules. Values of  $c$  and  $V_s$  in cubic feet per pound are tabulated for each  $1^\circ \text{C.}$  in Table III. Values of  $V$  for dry steam in terms of  $T$  and  $P$  are given in Table V.

*Expressions for  $E$  and  $H$  in terms of  $P$  and  $V$  for Dry Steam.*

$$E = (10/8) aP (V - b) + B,$$

$$H = E + aPV = (18/8) aP (V - b) + abP + B,$$

which gives for  $V$  in terms of  $H$  and  $P$ ,

$$V = 8 (H - B)/18aP + 10b/18,$$

whence  $V = 2.2486 (H - 464)/P + 0.0128$  (F.P.C.),

$$V = 1.2464 (H - 885.2)/P + 0.0128 \quad (\text{F.P.F.}),$$

$$V = 0.009847 (H - 464)/P + 0.00077 \quad (\text{K.M.C.}).$$

• *General Expression for the Entropy  $\Phi$  of Dry Steam at  $P$  and  $T$ .*

$$\Phi = 1.09876 \log (T/T_1) - .25356 \log (P/P_1) - a n c P/T + 1.76300.$$

where  $T_1, P_1$  are the values of  $T$  and  $P$  at the boiling-point.

The Entropy is the same in all three systems of units.

*Adiabatic or Isentropic Expansion of Dry Steam.* Adiabatic equation,

$$P(V - b)^{1.3} = \text{constant}, \quad \text{or } P(V - b)/T = \text{constant},$$

$$\text{or } P/T^{1.3/3} = \text{constant}, \quad \text{or } (V - b) T^{10/3} = \text{constant}.$$

*Heat-drop from  $H_0, P_0, V_0, T_0$ , in Isentropic Expansion of Dry Steam.*

$$\begin{aligned} (H_0 - H)_s &= (13/3) a P_0 (V_0 - b) (1 - (P/P_0)^{3/13}) + ab (P_0 - P) \\ &= (H_0 - B - abP_0) (1 - T/T_0) + ab (P_0 - P). \end{aligned}$$

*General Expression for Velocity  $U$  due to Heat-drop.*

$$U = (2Jg)^{1/2} (H_0 - H)^{1/2},$$

$$\text{which gives } U = 300.2 (H_0 - H)^{1/2} \text{ ft./sec.} \quad (\text{F.P.C.}),$$

$$\text{or } U = 223.8 (H_0 - H)^{1/2} \text{ ft./sec.} \quad (\text{F.P.F.}),$$

$$\text{or } U = 91.51 (H_0 - H)^{1/2} \text{ m./sec.} \quad (\text{K.M.C.}).$$

*Cross-section  $X$  of a Nozzle for Discharge of Mass  $M$  per second.*

$$X (\text{in.}^2) = 144 MV/U \quad (\text{F.P.C. or F.}),$$

$$X (\text{cm.}^2) = 10000 MV/U \quad (\text{K.M.C.}).$$

*Discharge  $M/X_1$  through a Nozzle per Unit Area of Throat  $X_1$  for Dry Steam.*

$$M/X_1 (\text{lbs./sec. in.}^2) = 0.8155 (1 + 0.274b/V_0) (P_0/V_0)^{1/2}, \quad (\text{F.P.C.}$$

$$\text{or F.})$$

$$M/X_1 (\text{kg./sec. cm.}^2) = 0.02090 (1 + 0.274b/V_0) (P_0/V_0)^{1/2} \quad (\text{K.M.C.}).$$

$$\text{Throat Pressure, } P_1/P_0 = 0.5457 - 0.139b/V_0.$$

(The  $b$  terms may be omitted in all the above formulae unless  $V$  is small.)

*Approximate Formula for Volume  $V_s$  of Dry Saturated Steam.*

$$pV_s^{1.3/15} = 490 \quad (\text{F.P.C. or F.}), \quad pV_s^{1.6/15} = 1.786 \quad (\text{K.M.C.}),$$

whence Discharge of Steam, initially dry and saturated, without condensation in the supersaturated state,

$$M/X_t = 0.01780 P_0^{31/32} \quad (\text{F.P.C. or F.}),$$

$$M/X_t = 0.01598 P_0^{31/32} \quad (\text{K.M.C.}).$$

*Approximate Equation (Zeuner) for Adiabatics of Wet Steam.*

$$pV^{1.035+0.1q} = \text{constant, where } q = \text{initial dryness fraction,}$$

whence Discharge of Steam initially dry, but with reversible condensation, according to the above formula,

$$P_t/P_0 = 0.577, \quad M/X_t = 0.01646 P_0^{31/32} \quad (\text{F.P.C. or F.}),$$

$$M/X_t = 0.01516 P_0^{31/32} \quad (\text{K.M.C.}).$$

*Gibbs' Function or Potential,  $G = T\Phi - H$ , for Steam in any State.*

For water or wet steam at  $t$ ,

$$G_s = T\phi - h = T\Phi_s - H_s = sT \log_e (T/T_0) - st - 0.003 t/T_0,$$

a function of the temperature only, tabulated in Table III, for each  $1^\circ \text{C.}$

The equation  $T\Phi - H = G_s$ , with  $H$  and  $\Phi$  for dry steam, determines the saturation pressure  $p$ .

The relation  $H = T\Phi - G_s$  is the exact equation for the adiabatics of wet steam when  $\Phi$  is constant, giving  $H$  directly in terms of  $t$  and  $\Phi$ . It may also be written in the forms,

$$\begin{aligned} H_s - H &= T(\Phi_s - \Phi) = (1 - q)L = (1 - q)(H_s - st)(1 - v/V_s) \\ &= (H_s - st)(V_s - V)/V_s^2, \end{aligned}$$

where  $H_s$ ,  $\Phi_s$ ,  $V_s$ , are for dry steam at  $t$ , and  $H$ ,  $\Phi$ ,  $V$ , for wet steam. The expressions in terms of  $q$  are not required unless the hypothetical value of  $q$  is one of the given data, or unless a diagram is employed which gives  $q$  only in place of giving  $V$  directly. The expression for the adiabatic heat-drop  $(H' - H'')_s$ , is obtained by taking the difference between the initial and final values of  $H$ ,

$$(H' - H'')_s = (t' - t'')\Phi' - (G' - G'') = H' - H_s'' + T''(\Phi_s'' - \Phi').$$

The first expression is general, and is most convenient for wet steam. The second applies only when the final state is wet.

*Rankine Cycle and Relative Efficiency F.* Thermal Equivalent  $AW$  of the work done in the cycle between limits  $p'$  and  $p''$

$$AW = (H' - H'')_s - a(p' - p'')v'' = (t' - t'')\Phi' - (G' - G'') - Aw.$$

Heat supplied,  $H' - h'' - Aw$ . Efficiency,  $AW/(H' - h'' - Aw)$ , where  $Aw = a(p' - p'')v''$ . The "Efficiency Ratio" is the ratio



calculating  $q$  or making any correction for  $v$ , or for the variation of the specific heat.

The external work of vaporisation,  $ap(V_g - v)$ , and the intrinsic energy  $E$ , are very seldom required, but are easily found from the tables of  $p$ ,  $V$ , and  $H$ .

The auxiliary quantities  $SC$  and  $Z = anc/T$  are useful in calculating  $H$  and  $C$ , or  $\Phi$  and  $S$ , respectively, but are also easily obtained from Table III ( $c$ ), giving  $c$  for each  $1^\circ \text{C.}$ , so that it is unnecessary to tabulate them more fully. The specific heat  $S$ , and the cooling-effect  $C$ , are so easily found from the table of total heat, that it is unnecessary to tabulate them separately, especially as their chief use is for calculating  $H$ .

Table II contains the most important properties of saturated steam tabulated in terms of pressure for all three systems of units, and will be found the most useful table for general purposes. Except for pressures below 1 lb. per sq. in. (which are altogether omitted in many steam tables) the intervals of pressure are graduated so that the corresponding intervals of temperature shall never exceed  $2^\circ \text{C.}$  or fall below  $1^\circ \text{C.}$ , which affords the most convenient scale for interpolation. The corresponding values of the pressure in kilos per sq. cm. in the second column are the exact equivalents to five significant figures of the pressures in lbs. per sq. in. in the first column. The values in both cases are for the latitude of London, and must be increased by 1 in 2000 if it is required to express them in terms of the conventional value of gravity in latitude  $45^\circ$ . This correction may generally be neglected, since it does not affect the relative values, and is beyond the limit of accuracy of most observations. It should not in any case be applied to individual observations, but only as a final correction to the results of a series.

The values of the volume in the third and fourth columns are given to four significant figures, i.e. with a *minimum* accuracy of 1 in 2000, corresponding to about  $0.01^\circ \text{C.}$  of temperature. More accurate values may be obtained, if required for small differences, from Table III ( $V$ ), for each  $1^\circ \text{C.}$  Owing to the great range of variation of the pressure and the volume, it is impossible to secure a uniform degree of proportionate accuracy in tabulating these quantities, except in the table of  $\log p$ .

The values of the entropy in the fifth column are the same in all three systems of units. They are seldom required for small differences, and are often tabulated to three places of decimals only.

The values of  $t$ ,  $H$ , and  $G$ , for saturated steam are tabulated in both Fahrenheit and Centigrade systems, to save the trouble of reduction to or from the Fahrenheit scale, which is the most annoying feature of the British system of units. The values are given to  $0.01^\circ$  of temperature and  $0.01$  of a heat unit respectively, because  $t$ ,  $H$ , and  $G$  are most often required for small differences, especially in deducing the heat-drop and velocity. It would for this reason be inconsistent to tabulate them (as in many other steam tables) with an order of accuracy inferior to that employed for the entropy.

The case of saturated steam is most completely covered for practical purposes by Table II, but the supplementary tables of  $p$ ,  $\log p$ ,  $V$ ,  $c$ ,  $H$ , and  $G$  for each  $1^\circ$  C. will be found useful in cases where it is desired to solve, to the limit of accuracy, problems in which the elimination cannot be effected so that it is necessary to proceed by trial and interpolation, as is generally the case in the solution of transcendental equations. Quadratic and cubic empirical formulæ are often employed in preference to logarithmic with the idea of avoiding this difficulty; but the advantage gained is fictitious, because it is generally much easier to solve a logarithmic formula by interpolation, than to find the solution, even of a quadratic, without the aid of logarithms.

With the exception of the formulæ for the saturation pressure and entropy, which cannot possibly be put in any form except the logarithmic if they are to satisfy the second law of thermodynamics, the equations expressing the relations between the various properties of saturated steam are of the simplest possible algebraic type, involving no powers or roots, and exceptionally convenient for practical calculations as compared with the ordinary type of empirical formula involving powers of the temperature.

**200. Tables for Superheated Steam.** The simplicity of the characteristic equation and the adiabatic equation for dry steam makes it possible to solve the majority of problems for superheated or supersaturated steam as easily as for a perfect gas. Tabulation is superseded for many purposes by direct solution of the equations. The variation of specific heat is too large to neglect even in rough work, and it is a great advantage to be able to take exact account of the variation in so simple and consistent a manner. It is also possible to tabulate the values of the required quantities to a higher order of accuracy than is attainable with empirics



formulae without risk of introducing inconsistencies in any of the thermodynamical relations. The tabulated values are useful chiefly in finding the initial state, when the final state is wet and the simple adiabatic for dry steam does not apply to the whole range of expansion. They are also useful in reducing experiments on the cooling-effect, and other relations of superheated steam.

The majority of problems relating to superheated steam may be solved with sufficient approximation for practical purposes by the aid of the diagram. The tables serve chiefly as a method of verification, and supply more accurate values in problems where small differences are involved. The arrangement of the tables, with the scale of temperature on the left, and pressure along the top, is intended to correspond with the diagram. The practical limit of temperature in the use of superheated steam is in the neighbourhood of  $400^{\circ}\text{C.}$ , which is comparatively seldom reached in the engine. The values tabulated for  $450^{\circ}$  and  $500^{\circ}\text{C.}$  are of theoretical rather than practical interest. Initial pressures below 50 lbs. are so uncommon, and below 20 lbs. so extremely rare, that close tabulation by steps of 1 lb. down to the lowest pressures (adopted in many steam tables) is quite superfluous in the case of superheated steam. The accuracy of the interpolation formulae given below makes it unnecessary to tabulate the values for intervals of less than 10 lbs. in any part of the range. Intervals of 50 lbs. suffice at the upper limit of pressure.

Owing to the comparatively limited utility of tables for superheated steam, it has not been considered worth while to duplicate them in terms of the Fahrenheit scale and metric units of pressure. Values on either of these systems can be obtained very readily, if required, by the aid of the Fahrenheit scale of temperature on the left, and the kilogram scale of pressure at the top of each table. This arrangement has been found more convenient in practice than duplicating the tables.

In experimental tests, the practical datum is always the temperature and not the superheat. If the superheat only is given, the actual temperature of the steam must be found by adding the saturation temperature which is given for each pressure at the bottom of the column. The saturation line in each table is indicated by a zigzag rule. Values below this line represent the state of supersaturation, which is of great theoretical interest, though not permanently stable. These values cannot occur as initial states, but only as transition states; and are useful chiefly for the purpose

of estimating possible losses due to irreversible condensation, or changes of volume in rapid expansion which materially affect the discharge through orifices.

### 201. Table IV. Total Heat of Superheated Steam.

The most useful table for superheated steam is that of total heat  $H$ , which is the chief factor in determining the heat supply per unit mass of fluid. It is very easy to obtain accurate values of  $H$  by interpolation because the variation with pressure at constant temperature is small, and is accurately represented by the *constant* difference tabulated for 10 lbs. of pressure in the third column of the table. If the exact value of  $H$  is required at some intermediate pressure and temperature, it is generally best, for this reason, to find (1) two values of  $H$  at the given pressure for tabulated values of the temperature immediately above and below the required point, and (2) to interpolate between these for the required temperature. But for most purposes ample accuracy is secured by adding simultaneously the appropriate fractions of the pressure and temperature differences to the nearest tabulated value of  $H$ .

The table of  $H$  affords the most convenient method of finding the specific heat  $S$  at any point, or the mean specific heat over any range. Values of the mean specific heat for various ranges are often tabulated for calculating  $H$  when the superheat is given, but the opposite procedure is more accurate and convenient. The difference between any two adjacent values of  $H$  in the same vertical column is 10 times the specific heat  $S$  at the mean point, which is directly obtained to 3 significant figures. Thus the value of  $S$  at 500 lbs. and 245° C. is  $(684.01 - 677.22)/10 = 0.679$ , and the mean value at the same pressure from 240° C. to 340° C. is

$$(739.46 - 677.22)/100 = 0.6224.$$

Another useful application of the table is to find the cooling-effect  $C$  at any point, which is obtained by dividing the difference  $SC$  per pound, by the corresponding value of  $S$  obtained as already described. Thus to find  $C$  at 500 lbs. and 245° C., we have  $SC = 0.06122$  by interpolation from the difference column,  $S = 0.679$  already found, whence  $C = 0.0902^\circ/\text{lb.}$  Similarly at 50 lbs. and 150° C.,  $S = 0.526$ ,  $SC = 0.1218$ ,  $C = 0.232^\circ/\text{lb.}$

The drop of temperature for a large drop of pressure at constant total heat, may be obtained by finding the temperature by interpolation at the lower pressure required to give the initial value of

the total heat. Thus  $H$  at  $200^\circ$  and 200 lbs. is 678.07, which is the value given by interpolation at  $176^\circ$  and 22.69 lbs., or at 20 lbs. and  $169.43^\circ$ . It is very easy to trace lines of constant total heat in this way.

202. Tables V, VI, and VII. Interpolation for  $V$ ,  $\Phi$ , and  $G$ . When the final state in adiabatic expansion is dry,  $T$ ,  $H$ , and  $V$  are easily calculated from the adiabatic equation in the same way as for a perfect gas, but the required result may often be obtained with less trouble from the tables by interpolation, if exact values are required. When the final pressure  $P''$  is given, find  $T''$  by interpolation in Table VI at  $P''$ . Thence find  $H''$  by interpolation in Table IV, and deduce  $V''$  from  $H''$  and  $P''$ , or by interpolation in Table V.

Accurate values at any point intermediate between the tabulated values may generally be obtained with a small slide-rule by simple proportion in the usual way, provided that the differences involved are small, but this rule is insufficiently exact for some purposes in the case of  $V$ ,  $\Phi$ , and  $G$ , when the pressure differences are considerable. The following rule is *exact* in the case of  $V$  at constant temperature, for any pressure difference, however large.

If  $V'$ ,  $V''$  are tabulated values of the volume at the same temperature  $T$ , corresponding to pressures  $P'$ ,  $P''$  (of which  $P''$  is the larger) to find the value of  $V$  at any pressure  $P$  intermediate between  $P'$  and  $P''$ , find the value of the difference

$$V' - V = (V' - V'') (P - P'') / (P'' - P')$$

by simple proportion in the usual way, increase it by the fraction  $(P'' - P)/P$  of itself, and subtract the result from  $V'$ .

In the case of  $\Phi$  and  $G$  a similar rule applies, but the corresponding difference,  $\Phi' - \Phi$ , or  $G' - G$ , found by simple proportion, must be increased by the fraction  $(P'' - P)/2P$  of itself (with  $2P$  in the denominator in place of  $P$ ) before subtraction from  $\Phi'$  or  $G'$ .

**Table VIII. Adiabatic Heat-Drop to 1 lb.** This table is fully explained and illustrated in Chapter IX, § 92, but has been placed with the other tables to facilitate reference.

## REFERENCES

Selected papers by the author and his collaborators bearing on the subject of the present work.

- (1) "On the Practical Measurement of Temperature," *Phil. Trans.*, 1887, vol. 178 A, pp. 161-230. Proposing the platinum thermometer as a practical or secondary standard, proving the formula given in Chapter I, § 7 for the difference between the platinum scale and the gas scale, and testing the law of variation of electrical resistance with temperature by comparing different metals with each other and with the air-thermometer.
- (2) "On the Boiling-point of Sulphur" (with E. H. Griffiths), *Phil. Trans.*, 1891, vol. 182 A, pp. 119-157. Using the same air-thermometer and platinum thermometer as in the previous investigation, the value found for the boiling-point of sulphur was  $444.53^{\circ}\text{C}$ ., which has since been verified (e.g. by Eumorfopoulos, *Proc. R. S.*, 1914, vol. 90 A, pp. 189-203), and is now generally accepted as a convenient fixed point for testing thermometers.
- (3) "On a Compensated Air-Thermometer," *Proc. R. S.*, vol. 50 A, pp. 247-251. Describing a delicate type of gas-thermometer, capable of reading to  $1/4000$  of  $1^{\circ}\text{C}$ ., and specially suited for work of precision (Preston's *Heat*, p. 136).
- (4) "On the Construction of Platinum Thermometers," *Phil. Mag.*, July 1891, pp. 104-113. Explaining methods of making and testing thermometers, and describing a suitable form of apparatus for taking readings. Most of the investigations enumerated below would have been impossible to carry out successfully without thermometers of this type.
- (5) "On the Variation of the Electromotive Force of the Clark Standard Cell with Temperature and with strength of Solution" (with H. T. Barnes), *Proc. R. S.*, 1897, vol. 62, pp. 117-152. This was required for using the Clark cell as a standard for measuring electric energy in calorimetric experiments.
- (6) "On the Law of Condensation of Steam" (with Prof. J. T. Nicolson), *Proc. Inst. C. E.*, 1897-8, vol. 131, pp. 1-126. The law was deduced from measurements of temperature-cycles of the walls and steam in the cylinder of a steam-engine. The paper also describes experiments on valve-leakage, and on conduction of heat in cast iron, and discusses the effect of various conditions, such as superheat and supersaturation, on cylinder condensation.
- (7) "An Electrical Method of measuring the Temperature of a Metal Surface on which steam is condensing," *Brit. Assoc. Rep.*, 1897, p. 422. An independent method of verifying the law of condensation.
- (8) "Continuous Electric Method of determining the Specific Heat of a Liquid" (with H. T. Barnes), *Brit. Assoc. Rep.*, 1897, p. 552. Giving a general description of the method, with illustrative results for mercury.
- (9) "On the Variation of the Specific Heat of Water" (with H. T. Barnes), *Brit. Assoc. Rep.*, 1899, pp. 624-632. Giving preliminary details and results of the continuous electric method as applied to water.
- (10) "Notes on Platinum Thermometry," *Phil. Mag.*, Feb. 1899, pp. 101-222. Answering some objections to the method, and discussing later developments especially at high and low temperatures.
- (11) "Thermodynamical Properties of Gases and Vapours, deduced from a modified form of the Joule-Thomson Equation, with special reference to the properties of Steam," *Proc. R. S.*, 1900, vol. 67 A, pp. 286-286 (*R. S.*, 1900). Giving general expressions for the variation of the total heat, specific heats, entropy, and

saturation pressure, according to the characteristic equation assumed, illustrated by tables of the properties of steam as originally calculated with Maxwell's theoretical value 4.5 for the ratio  $S/R$  in the case of a triatomic vapour. The value 4.33 for steam, previously deduced from experiments on the adiabatic index, was subsequently confirmed by more accurate experiments on the specific heat, and employed in the revised tables.

(12) *Encyclopædia Britannica*, 10th edition (*E. B.*, 1902). Articles on Calibration, Calorimetry, Conduction of Heat, Fusion, Thermodynamics, Thermoelectricity, Thermometry, and Vaporization. Giving details of the chief experimental and theoretical methods of deducing the thermal properties of substances, and the fundamental constants required in the theory of heat. Revised data for steam were given, including the new definition of total heat and the formula for the total heat of water, which showed improved agreement with experiment. The same articles were republished in the 11th edition, 1910, with the addition of a general article on Heat, illustrating the development of the theory, especially in its application to heat-engines.

(13) "Continuous Electric Calorimetry," *Phil. Trans.*, 1902, vol. 199 A, pp. 55-148. Giving a full account of the theory of the method, and of the final corrections to be applied in reducing the results, including the determination of the absolute electromotive force of the Clark cells by R. O. King with a special electrodynamicometer. The details of the observations on the variation of the specific heat of water were given in a separate paper by H. T. Barnes (*loc. cit.*, pp. 149-203), having been completed after the author had left McGill University.

(14) "On the Thermodynamical Correction of the Gas-Thermometer," *Phil. Mag.*, Jan. 1903, pp. 48-65. Explaining the application of the characteristic equation (*R. S.*, 1900) to other gases, and the deduction of the required coefficients from observations of the specific heat and cooling-effect, and giving tables of corrections to be applied in reducing observations with various gas-thermometers to the absolute thermodynamic scale.

(15) "On the Osmotic Pressure and Vapour-Pressure of Strong Solutions," *Proc. R. S.*, 1908, vol. 80 A, pp. 466-500. Giving the general theory of the variation of the vapour-pressure of a liquid with capillary pressure, which is the cause of the phenomena of supersaturation, with applications to aqueous solutions, by the methods of the isothermal circuit and cycle.

(16) "First Report of the Committee on Gaseous Explosions," *Brit. Assoc. Rep.*, 1908, pp. 1-33. Discussing later experimental results with regard to the variation of the specific heats of gases and vapours.

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(18) "On the Variation of the Specific Heat of Water, with Experiments by a New Method," Bakerian Lecture, *Phil. Trans.*, 1912, vol. 212 A, pp. 1-32. The variation found by the continuous electric method had been disputed by later experimentalists, but was closely confirmed by the continuous mixture method described in the above paper.

(19) "On the Steady Flow of Steam through a Nozzle or Throttle," *Proc. Inst. Mech. Eng.*, Feb. 1915, pp. 53-77. Giving equations and formulae for the discharge of steam, with special reference to the effects of supersaturation and friction.

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## TABLES I–IX

**TABLE I.—AUXILIARY TABLE FOR SATURATED STEAM OF QUANTITIES  
SELDOM REQUIRED, IN TERMS OF TEMPERATURE CENTIGRADE IN  
FOOT-POUND UNITS. (F.P.C.)**

<i>t</i>	<i>h</i>	<i>L</i>	<i>AW</i>	<i>E</i>	$\phi$	$\Phi$	<i>v</i>	<i>SC</i>	1000 <i>Z</i>
0	0	594.27	30.063	564.21	0	2.17602	0.01802	0.5295	1.496
10	9.98	589.03	31.156	567.85	0.03585	2.11649	0.01603	0.4695	1.280
20	19.94	583.78	32.243	571.48	0.07046	2.06221	0.01605	0.4181	1.102
30	29.91	578.46	33.324	575.07	0.10393	2.01247	0.01609	0.3736	0.9526
40	39.89	573.15	34.395	578.64	0.13631	1.96688	0.01614	0.3351	0.8275
50	49.88	567.75	35.455	582.17	0.16770	1.92490	0.01621	0.3016	0.7221
60	59.87	562.29	36.498	585.66	0.19815	1.88621	0.01629	0.2723	0.6327
70	69.88	556.72	37.523	589.07	0.22774	1.85039	0.01638	0.2466	0.5566
80	79.90	551.05	38.526	592.41	0.25652	1.81712	0.01648	0.2240	0.4914
90	89.94	545.25	39.502	595.67	0.28454	1.78619	0.01659	0.2039	0.4354
100	100.00	539.30	40.448	598.83	0.31186	1.75732	0.01671	0.1861	0.3871
110	110.09	533.17	41.361	601.86	0.33853	1.73027	0.01684	0.1703	0.3452
120	120.22	526.85	42.236	604.78	0.36460	1.70485	0.01698	0.1561	0.3087
130	130.40	520.32	43.072	607.58	0.39011	1.68092	0.01713	0.1435	0.2768
140	140.62	513.57	43.864	610.23	0.41511	1.65831	0.01729	0.1321	0.2489
150	150.91	506.56	44.617	612.73	0.43963	1.63689	0.01746	0.1219	0.2245
160	161.26	499.29	45.311	615.08	0.46373	1.61657	0.01765	0.1126	0.2029
170	171.69	491.75	45.962	617.37	0.48743	1.59724	0.01785	0.1042	0.1838
180	182.21	483.93	46.564	619.30	0.51078	1.57884	0.01807	0.0966	0.1668
190	192.83	475.82	47.115	621.10	0.53381	1.56128	0.01831	0.0897	0.1517
200	203.55	467.41	47.617	622.91	0.55654	1.54453	0.01856	0.0834	0.1383
210	214.40	458.69	48.070	624.48	0.57904	1.52851	0.01885	0.0777	0.1263
220	225.37	449.69	48.474	625.93	0.60128	1.51326	0.01914	0.0725	0.1156
230	236.49	440.38	48.831	627.23	0.62332	1.49868	0.01946	0.0677	0.1060
240	247.74	430.81	49.147	628.43	0.64517	1.48480	0.01980	0.0633	0.0973
250	259.16	420.96	49.410	629.53	0.66687	1.47161	0.02016	0.0592	0.0895

**NOTATION AND FORMULÆ FOR THE VARIOUS QUANTITIES IN TABLE I.**

- h* = Total Heat of Water under saturation pressure *p*, in mean calories Centigrade.  
 $= st + vL/(V - v) = st + (H - st)v/V = H - L$ , in which the symbols denote:—  
*H* = Total Heat of Dry Steam at *p*, in mean calories Centigrade =  $S_0T - SC_1 + 464$ .  
*s* = Minimum Specific Heat of Water = 0.99666.  $st = t - t/300$ .  
*v* = Volume of Water, *V* = Volume of Dry Steam, at *p* in cubic feet per pound.  
The Ratio  $v/V = p/25000$  (nearly) if *p* is in pounds per sq. inch absolute.  
*L* = Latent Heat of Steam in mean calories Centigrade =  $(H - st)(1 - v/V)$ .  
*AW* = Thermal Equivalent in mean calories Centigrade of External Work of Vaporisation *W*.  
 $= ap(V - v)$ , where  $A = 1/J = 1/1400$ , and  $a = 144/1400$ , for (F.P.C.) units.  
*E* = Intrinsic Energy of Dry Steam at *p* in mean cal. C. =  $H - apV = aap(V - b) + 464$ .  
 $\phi$  = Entropy of Water at *p* in cal./deg. =  $s \log_e(T/273.1) + vL/T(V - v)$ .  
 $\Phi$  = Entropy of Dry Steam at *p* in cal./deg. =  $\phi + L/T$ .  
*SC* = Product of Specific Heat *S* of Steam and Cooling Effect *C*, in cal. per lb. pressure.  
 $= a(n + 1)c - ab$ , where  $b = v_0 = 0.01602$ ,  $c = 0.4213(373.1/T)^n$ , and  $n = 10/3$ .  
*Z* =  $anc/T$ .  $S = S_0 + (n + 1)Zp$ .  $S_0 = 0.47719 = (n + 1)R$ .  $R = 0.11012$  mean cal./deg.

**TABLE II.—PROPERTIES OF SATURATED STEAM IN TERMS OF PRESSURE (p)  
FOR KILOGRAMMETRE AND FOOT-POUND UNITS, CENTIGRADE AND  
FAHRENHEIT. (K.M.C.), (F.P.C.), and (F.P.F.)**

Pressure p.		Volume V.		Entropy $\Phi$ C. or F.	Temperature t, Total heat H, and Potential G.					
Pounds Sq. in.	Kilos Sq. cm.	Cu. ft. Pound	Cu. m. Kilo.		Centigrade units.			Fahrenheit units.		
					t	H	G	t	H	G
0.08922	0.00627	3276	204.5	2.1760	0°	594.27	0	32°	1069.70	0
0.1	0.00703	2940	183.5	2.1662	1.59	595.03	0.006	34.86	1071.06	0.009
0.2	0.01406	1524	95.17	2.1068	11.09	599.81	0.246	53.04	1079.06	0.443
0.3	0.02109	1038	64.78	2.0727	17.99	602.77	0.58	64.38	1084.99	1.04
0.4	0.02812	790.7	49.36	2.0482	22.66	604.97	0.91	72.79	1088.95	1.64
0.5	0.03515	640.5	40.61	2.0299	26.41	606.73	1.23	79.54	1092.12	2.21
0.6	0.04218	539.1	33.66	2.0148	29.54	608.19	1.53	85.17	1094.74	2.75
0.7	0.04921	466.2	29.11	2.0018	32.25	609.44	1.82	90.05	1096.99	3.28
0.8	0.05625	411.1	25.66	1.9906	34.65	610.55	2.10	94.36	1098.99	3.78
0.9	0.06328	367.9	22.97	1.9810	36.83	611.58	2.37	98.30	1100.84	4.27
1.0	0.07031	333.1	20.79	1.9724	38.74	612.55	2.61	101.74	1102.43	4.70
1.1	0.07734	304.5	19.01	1.9646	40.52	613.28	2.85	104.94	1103.90	5.13
1.2	0.08437	280.0	17.52	1.9575	42.17	614.04	3.08	107.91	1105.27	5.54
1.3	0.09140	260.2	16.24	1.9509	43.71	614.75	3.31	110.68	1106.55	5.96
1.4	0.09843	242.7	15.15	1.9449	45.14	615.41	3.52	113.25	1107.74	6.33
1.5	0.10546	227.4	14.19	1.9392	46.49	616.02	3.73	115.69	1108.84	6.71
1.6	0.11249	214.0	13.36	1.9339	47.77	616.61	3.93	117.98	1109.90	7.08
1.7	0.11952	202.2	12.63	1.9290	48.98	617.16	4.13	120.17	1110.89	7.44
1.8	0.12655	191.6	11.96	1.9244	50.13	617.69	4.32	122.23	1111.85	7.78
1.9	0.13358	182.1	11.37	1.9200	51.22	618.19	4.51	124.20	1112.74	8.12
2.0	0.14061	173.5	10.83	1.9159	52.27	618.67	4.69	126.08	1113.61	8.45
2.2	0.15468	158.7	9.906	1.9081	54.24	619.55	5.03	129.64	1115.20	9.06
2.4	0.16874	146.4	9.140	1.9010	56.06	620.36	5.37	132.92	1116.65	9.67
2.6	0.18280	135.6	8.466	1.8947	57.75	621.14	5.69	135.94	1118.05	10.24
2.8	0.19686	126.5	7.897	1.8888	59.34	621.86	6.00	138.82	1119.35	10.80
3.0	0.21092	118.6	7.401	1.8833	60.83	622.53	6.30	141.50	1120.56	11.34
3.2	0.22498	111.6	6.967	1.8780	62.24	623.16	6.58	144.04	1121.69	11.84
3.4	0.23904	105.4	6.582	1.8731	63.58	623.76	6.86	146.44	1122.77	12.35
3.6	0.25311	99.93	6.238	1.8685	64.85	624.32	7.13	148.73	1123.78	12.83
3.8	0.26717	95.00	5.930	1.8641	66.07	624.87	7.39	150.92	1124.77	13.30
4.0	0.28123	90.54	5.652	1.8600	67.23	625.38	7.64	153.01	1125.69	13.75

$T = t + 273.10^\circ$  Centigrade.  $T = t + 459.58^\circ$  Fahrenheit.  $G = T\Phi - H$ .

Adiabatic Heat-Drop.  $H' - H'' = (t' - t'')\Phi' - (G' - G'') = (H' - H'') + T''(\Phi' - \Phi'')$ .

The suffix, in  $H$ ,  $V$ , or  $\Phi$ , denotes the tabulated saturation value at  $t$  or  $p$ .

To find  $H$  and  $V$  for wet steam, given  $\Phi$ , and  $t$  or  $p$ ,

$H_s - H = T(\Phi_s - \Phi)$ , or  $H = T\Phi - G$ ,

$V_s - V = V_s(H_s - H)/(H_s - s(t - 32))$  Fahr.



**TABLE II.—PROPERTIES OF SATURATED STEAM IN TERMS OF PRESSURE (p)  
FOR KILOGRAMMETRE AND FOOT-POUND UNITS, CENTIGRADE AND  
FAHRENHEIT.**

Pressure p.		Volume V.		Entropy $\Phi$ C. or F.	Temperature t, Total heat H, and Potential G.					
Pounds Sq. in.	Kiloes Sq. cm.	Cu. ft. Pounds	Cu. m. Kiloe		Centigrade units.			Fahrenheit units.		
					t	H	G	t	H	G
4.0	0.28123	90.54	5.652	1.8600	67.23	625.38	7.64	153.01	1125.69	13.75
4.2	0.29529	86.50	5.400	1.8561	68.34	625.87	7.89	155.01	1126.57	14.20
4.4	0.30935	82.80	5.169	1.8524	69.40	626.34	8.12	156.92	1127.41	14.62
4.6	0.32341	79.42	4.958	1.8489	70.43	626.79	8.36	158.77	1128.23	15.05
4.8	0.33747	76.31	4.764	1.8455	71.42	627.22	8.59	160.55	1129.00	15.46
5.0	0.35154	73.44	4.585	1.8422	72.38	627.64	8.81	162.28	1129.75	15.86
5.2	0.36560	70.80	4.420	1.8391	73.30	628.03	9.03	163.94	1130.46	16.25
5.4	0.37966	68.34	4.266	1.8361	74.19	628.42	9.25	165.54	1131.16	16.65
5.6	0.39372	66.05	4.123	1.8331	75.06	628.81	9.46	167.11	1131.86	17.03
5.8	0.40778	63.91	3.990	1.8303	75.90	629.17	9.66	168.62	1132.51	17.39
6.0	0.42184	61.91	3.865	1.8277	76.72	629.52	9.86	170.09	1133.15	17.75
6.5	0.45700	57.44	3.586	1.8214	78.67	630.37	10.34	173.60	1134.67	18.61
7.0	0.49215	53.59	3.346	1.8156	80.49	631.15	10.81	176.88	1136.07	19.46
7.5	0.52730	50.24	3.134	1.8101	82.21	631.88	11.25	179.98	1137.38	20.25
8.0	0.56246	47.30	2.953	1.8049	83.84	632.57	11.69	182.91	1138.63	21.04
8.5	0.59761	44.69	2.790	1.8000	85.38	633.23	12.10	185.68	1139.82	21.78
9.0	0.63276	42.36	2.644	1.7956	86.84	633.85	12.50	188.31	1140.94	22.50
9.5	0.66792	40.27	2.520	1.7914	88.24	634.44	12.89	190.84	1141.99	23.20
10.0	0.70307	38.39	2.397	1.7874	89.58	635.01	13.26	193.25	1143.02	23.87
10.5	0.73822	36.68	2.290	1.7836	90.87	635.54	13.63	195.57	1143.98	24.54
11.0	0.77338	35.11	2.192	1.7799	92.10	636.05	13.99	197.78	1144.89	25.18
11.5	0.80853	33.68	2.103	1.7765	93.29	636.55	14.33	199.92	1145.79	25.79
12.0	0.84368	32.37	2.021	1.7731	94.44	637.02	14.67	201.99	1146.64	26.40
12.5	0.87884	31.15	1.945	1.7699	95.55	637.47	15.00	203.99	1147.45	27.00
13.0	0.91399	30.03	1.875	1.7669	96.62	637.91	15.32	205.92	1148.24	27.57
13.5	0.94914	28.99	1.810	1.7640	97.66	638.35	15.63	207.78	1149.03	28.13
14.0	0.98430	28.02	1.749	1.7611	98.66	638.77	15.94	209.59	1149.80	28.69
14.5	1.0195	27.11	1.693	1.7584	99.64	639.16	16.25	211.34	1150.49	29.25
14.689	1.0327	26.70	1.672	1.7573	100°	639.30	16.36	212°	1150.74	29.45
15.0	1.0546	26.27	1.640	1.7557	100.58	639.53	16.54	213.05	1151.16	29.77
16.0	1.1249	24.73	1.544	1.7506	102.41	640.26	17.12	216.34	1152.43	30.82
17.0	1.1952	23.37	1.450	1.7458	104.14	640.95	17.68	219.46	1153.72	31.82
18.0	1.2655	22.16	1.383	1.7414	105.79	641.60	18.20	222.42	1154.88	32.76
19.0	1.3358	21.06	1.315	1.7373	107.36	642.22	18.72	225.24	1156.00	33.69
20.0	1.4061	20.08	1.253	1.7333	108.87	642.82	19.22	227.97	1157.08	34.59

$T = t + 273.10^\circ$  Centigrade.  $T = t + 459.68^\circ$  Fahrenheit.  $G = T\Phi - H$ .

Adiabatic Heat-Drop.  $H' - H'' = (t' - t'') \Phi' - (G' - G'') = (H' - H'') + T''(\Phi' - \Phi'')$ .

The suffix  $s$  in  $H_s$ ,  $V_s$ , or  $\Phi_s$  denotes the tabulated saturation value at  $t$  or  $p$ .

**TABLE II.—PROPERTIES OF SATURATED STEAM IN TERMS OF PRESSURE (*p*)  
FOR KILOGRAMMETRE AND FOOT-POUND UNITS, CENTIGRADE AND  
FAHRENHEIT.**

Pressure <i>p</i> .		Volume <i>V</i> .		Entropy $\Phi$ C. or F.	Temperature <i>t</i> , Total heat <i>H</i> , and Potential <i>G</i> .					
Pounds sq. in. •	Kilos. Sq. cm.	Cu. ft. Pound	C <sup>o</sup> . m. Kilo		Centigrade units.			Fahrenheit units.		
					<i>t</i>	<i>H</i>	<i>G</i>	<i>t</i>	<i>H</i>	<i>G</i>
20	1.4061	20.08	1.253	1.7333	108.87	612.82	19.22	227.97	1157.08	34.69
21	1.4764	19.18	1.197	1.7294	110.32	643.39	19.71	230.58	1158.10	35.48
22	1.5408	18.37	1.147	1.7258	111.71	643.92	20.18	233.08	1159.76	36.32
23	1.6171	17.62	1.100	1.7223	113.05	644.43	20.64	235.49	1159.98	37.15
24	1.6874	16.93	1.057	1.7189	114.34	644.93	21.09	237.81	1160.88	37.96
25	1.7577	16.29	1.017	1.7157	115.59	645.39	21.53	240.06	1161.70	38.75
26	1.8280	15.71	0.9801	1.7126	116.80	645.85	21.95	242.24	1162.53	39.51
27	1.8983	15.16	0.9464	1.7097	117.97	646.32	22.37	244.35	1163.38	40.27
28	1.9686	14.66	0.9149	1.7069	119.11	646.74	22.78	246.40	1164.14	41.00
29	2.0389	14.18	0.8854	1.7042	120.21	647.15	23.18	248.38	1164.88	41.72
30	2.1092	13.74	0.8577	1.7016	121.28	647.54	23.56	250.30	1165.58	42.41
31	2.1795	13.33	0.8319	1.6991	122.33	647.92	23.95	252.19	1166.26	43.11
32	2.2498	12.94	0.8076	1.6966	123.36	648.30	24.33	254.03	1166.94	43.79
33	2.3201	12.57	0.7847	1.6943	124.33	648.66	24.69	255.79	1167.60	44.44
34	2.3904	12.22	0.7631	1.6919	125.31	649.02	25.07	257.56	1168.24	45.12
35	2.4607	11.90	0.7426	1.6897	126.25	649.36	25.43	259.25	1168.86	45.77
36	2.5311	11.59	0.7234	1.6874	127.17	649.69	25.77	260.91	1169.44	46.38
37	2.6014	11.29	0.7051	1.6852	128.07	650.02	26.12	262.52	1170.04	47.01
38	2.6717	11.02	0.6876	1.6831	128.96	650.34	26.45	264.13	1170.61	47.61
39	2.7420	10.75	0.6711	1.6811	129.82	650.65	26.79	265.67	1171.17	48.22
40	2.8123	10.50	0.6554	1.6792	130.67	650.95	27.12	267.21	1171.71	48.81
42	2.9529	10.03	0.6261	1.6754	132.31	651.53	27.76	270.16	1172.76	49.97
44	3.0935	9.603	0.5994	1.6719	133.89	652.08	28.40	273.00	1173.74	51.12
46	3.2341	9.212	0.5750	1.6685	135.41	652.61	29.00	275.74	1174.70	52.20
48	3.3747	8.853	0.5527	1.6651	136.88	653.12	29.59	278.38	1175.62	53.26
50	3.5154	8.520	0.5319	1.6620	138.30	653.60	30.16	280.94	1176.48	54.29
52	3.6560	8.213	0.5127	1.6589	139.67	654.08	30.72	283.41	1177.35	55.29
54	3.7966	7.928	0.4949	1.6561	141.01	654.53	31.27	285.82	1178.15	56.28
56	3.9372	7.663	0.4784	1.6533	142.31	654.95	31.81	288.16	1178.91	57.26
58	4.0778	7.415	0.4629	1.6506	143.57	655.37	32.34	290.42	1179.67	58.21
60	4.2184	7.184	0.4485	1.6479	144.79	655.77	32.85	292.61	1180.39	59.13
62	4.3590	6.966	0.4348	1.6453	145.98	656.16	33.36	294.76	1181.08	60.05
64	4.4996	6.761	0.4221	1.6429	147.14	656.55	33.86	296.85	1181.79	60.95
66	4.6402	6.571	0.4102	1.6405	148.27	656.91	34.34	298.88	1182.44	61.81
68	4.7809	6.388	0.3988	1.6382	149.38	657.26	34.82	300.88	1183.07	62.68
70	4.9215	6.218	0.3882	1.6359	150.46	657.61	35.30	302.83	1183.70	63.54

To find *H* and *V* for wet steam, given  $\Phi$ , and *t* or *p*,

$$H_s - H = T(\Phi_s - \Phi), \text{ or } H = T\Phi - G.$$

$$V_s - V = V_s(H_s - H)/(H_s - s t)^\circ \text{Cent.} = V_s(H_s - H)/(H_s - s(t - 32))^\circ \text{Fahr.}$$

**TABLE II.—PROPERTIES OF SATURATED STEAM IN TERMS OF PRESSURE (p)  
• FOR KILOGRAMMETRE AND FOOT-POUND UNITS, CENTIGRADE AND  
FAHRENHEIT.**

Pressure p.		Volume V.		Entropy $\Phi$ C. or F.	Temperature t, Total heat H, and Potential G.					
Pounds Sq. in.	Kilos Sq. cm.	Cu. ft. Found	Cu. m. Kilo		Centigrade units.			Fahrenheit units.		
					t	H	G	t	H	G
70	4.9215	6.218	0.3882	1.6359	150.46	657.61	35.30	302.83	1183.70	63.54
72	5.0621	6.056	0.3781	1.6337	151.51	657.94	35.76	304.72	1184.29	64.36
74	5.2027	5.902	0.3685	1.6315	152.55	658.28	36.22	306.60	1184.90	65.18
76	5.3433	5.757	0.3594	1.6294	153.56	658.59	36.67	308.40	1185.46	66.01
78	5.4839	5.618	0.3507	1.6275	154.55	658.90	37.11	310.19	1186.03	66.80
80	5.6246	5.487	0.3425	1.6256	155.52	659.20	37.54	311.93	1186.56	67.57
82	5.7652	5.362	0.3348	1.6237	156.47	659.49	37.97	313.65	1187.08	68.34
84	5.9058	5.241	0.3272	1.6218	157.40	659.77	38.39	315.32	1187.59	69.10
86	6.0464	5.127	0.3201	1.6200	158.32	660.06	38.81	316.98	1188.11	69.85
88	6.1870	5.018	0.3133	1.6183	159.22	660.33	39.22	318.60	1188.60	70.60
90	6.3276	4.913	0.3067	1.6165	160.09	660.59	39.62	320.16	1189.06	71.30
92	6.4682	4.813	0.3004	1.6148	160.96	660.85	40.02	321.73	1189.53	72.04
94	6.6088	4.717	0.2945	1.6131	161.82	661.11	40.42	323.28	1190.00	72.76
96	6.7495	4.624	0.2887	1.6115	162.66	661.35	40.81	324.79	1190.43	73.46
98	6.8901	4.535	0.2831	1.6098	163.48	661.59	41.20	326.26	1190.86	74.16
100	7.0307	4.451	0.2779	1.6082	164.28	661.82	41.58	327.70	1191.28	74.84
105	7.3822	4.251	0.2654	1.6044	166.25	662.38	42.50	331.25	1192.29	76.50
110	7.7338	4.070	0.2541	1.6007	168.15	662.93	43.40	334.67	1193.27	78.12
115	8.0853	3.903	0.2437	1.5972	169.98	663.44	44.28	337.96	1194.19	79.70
120	8.4368	3.751	0.2342	1.5938	171.75	663.92	45.13	341.15	1195.06	81.22
125	8.7884	3.609	0.2254	1.5906	173.47	664.40	45.97	344.25	1195.92	82.75
130	9.1399	3.479	0.2172	1.5875	175.13	664.83	46.78	347.23	1196.69	84.20
135	9.4914	3.358	0.2096	1.5846	176.74	665.27	47.59	350.13	1197.49	85.66
140	9.8430	3.245	0.2026	1.5818	178.31	665.69	48.37	352.96	1198.24	87.07
145	10.195	3.140	0.1960	1.5791	179.83	666.10	49.13	355.69	1198.98	88.44
150	10.546	3.041	0.1898	1.5765	181.31	666.49	49.89	358.36	1199.68	89.80
155	10.898	2.949	0.1841	1.5740	182.75	666.86	50.62	360.95	1200.35	91.12
160	11.249	2.862	0.1787	1.5715	184.16	667.22	51.34	363.48	1200.99	92.41
165	11.601	2.781	0.1736	1.5691	185.54	667.56	52.05	365.97	1201.61	93.69
170	11.952	2.703	0.1687	1.5666	186.88	667.90	52.75	368.39	1202.22	94.95
175	12.304	2.631	0.1642	1.5643	188.19	668.22	53.43	370.74	1202.79	96.17
180	12.655	2.562	0.1600	1.5620	189.48	668.53	54.10	373.06	1203.35	97.38
185	13.007	2.496	0.1558	1.5598	190.74	668.83	54.77	375.33	1203.89	98.59
190	13.358	2.435	0.1520	1.5577	191.97	669.13	55.42	377.56	1204.44	99.76
195	13.710	2.376	0.1483	1.5557	193.18	669.41	56.07	379.72	1204.94	100.93
200	14.061	2.320	0.1448	1.5538	194.35	669.69	56.69	381.83	1205.44	102.04

$T = t + 273.10^\circ$  Centigrade.  $T = t + 459.68^\circ$  Fahrenheit.  $G = T\Phi - H$ .

Adiabatic Heat-Drop.  $H' - H'' = (t' - t'')\Phi' - (G' - G'') = (H' - H'') + T''(\Phi'' - \Phi')$ .

The suffix , in  $H$ ,  $V$ , or  $\Phi$  denotes the tabulated saturation value at  $t$  or  $p$ .

**TABLE II.—PROPERTIES OF SATURATED STEAM IN TERMS OF PRESSURE (p),  
FOR KILOGRAMMETRE AND FOOT-POUND UNITS, CENTIGRADE AND  
FAHRENHEIT.**

Pressure p.		Volume V.		Entropy $\Phi$ C. or F.	Temperature t, Total heat H, and Potential G.					
Pounds Sq. in.	Kilos Sq. cm.	Cu. ft. Pound	Cu. m. Kilo		Centigrade units.			Fahrenheit units.		
					t	H	G	t	H	G
200	14.061	2.320	0.1448	1.5538	194.35	669.69	56.69	381.83	1205.44	102.04
205	14.413	2.266	0.1415	1.5520	195.52	669.95	57.32	383.94	1205.61	103.18
210	14.764	2.216	0.1383	1.5502	196.66	670.20	57.94	385.98	1205.76	104.29
215	15.116	2.167	0.1353	1.5483	197.77	670.46	58.53	387.98	1205.83	105.35
220	15.468	2.120	0.1324	1.5465	198.87	670.70	59.13	389.97	1205.90	106.43
225	15.819	2.076	0.1296	1.5447	199.95	670.95	59.72	391.91	1207.71	107.50
230	16.171	2.034	0.1270	1.5429	201.02	671.19	60.31	393.84	1208.14	108.56
235	16.522	1.993	0.1244	1.5412	202.06	671.43	60.88	395.71	1208.56	109.68
240	16.874	1.954	0.1220	1.5395	203.09	671.64	61.45	397.56	1208.95	110.61
245	17.225	1.916	0.1196	1.5379	204.10	671.86	62.02	399.38	1209.35	111.63
250	17.577	1.880	0.1173	1.5362	205.10	672.07	62.59	401.18	1209.73	112.64
260	18.280	1.811	0.1131	1.5332	207.01	672.48	63.66	404.67	1210.47	114.59
270	18.983	1.748	0.1091	1.5303	208.93	672.88	64.72	408.08	1211.18	116.49
280	19.686	1.689	0.1055	1.5274	210.77	673.25	65.77	411.39	1211.85	118.38
290	20.389	1.634	0.1020	1.5246	212.57	673.61	66.79	414.63	1212.50	120.22
300	21.092	1.583	0.0988	1.5219	214.33	673.96	67.80	417.78	1213.13	122.04
310	21.795	1.534	0.0958	1.5192	216.02	674.29	68.79	420.84	1213.72	123.82
320	22.498	1.489	0.0930	1.5167	217.68	674.62	69.75	423.82	1214.32	125.55
330	23.201	1.446	0.0903	1.5142	219.30	674.93	70.70	426.74	1214.88	127.26
340	23.904	1.406	0.0878	1.5119	220.89	675.23	71.64	429.60	1215.41	128.95
350	24.607	1.368	0.0854	1.5096	222.45	675.52	72.57	432.41	1215.94	130.63
360	25.311	1.333	0.0832	1.5074	223.97	675.80	73.47	435.15	1216.44	132.24
370	26.014	1.298	0.0811	1.5053	225.45	676.07	74.36	437.81	1216.93	133.85
380	26.717	1.266	0.0790	1.5032	226.91	676.34	75.24	440.44	1217.41	135.43
390	27.420	1.235	0.0771	1.5012	228.34	676.59	76.09	443.01	1217.86	136.96
400	28.123	1.206	0.0753	1.4991	229.75	676.84	76.96	445.55	1218.32	138.53
410	28.826	1.178	0.0736	1.4971	231.13	677.07	77.80	448.04	1218.73	140.04
420	29.529	1.152	0.0719	1.4952	232.49	677.30	78.63	450.49	1219.14	141.63
430	30.232	1.127	0.0703	1.4933	233.82	677.53	79.44	452.88	1219.55	142.99
440	30.935	1.102	0.0688	1.4915	235.13	677.76	80.26	455.23	1219.97	144.46
450	31.638	1.079	0.0674	1.4897	236.42	677.97	81.06	457.55	1220.35	145.90
460	32.341	1.057	0.0660	1.4880	237.69	678.18	81.85	459.84	1220.73	147.33
470	33.044	1.036	0.0647	1.4863	238.93	678.38	82.63	462.08	1221.09	148.73
480	33.747	1.016	0.0634	1.4846	240.16	678.58	83.40	464.29	1221.44	150.12
490	34.450	0.996	0.0622	1.4830	241.37	678.78	84.16	466.47	1221.80	151.48
500	35.154	0.977	0.0610	1.4814	242.57	678.97	84.92	468.63	1222.15	152.86

To find  $H$  and  $V$  for wet steam, given  $\Phi$ , and  $t$  or  $p$ ,

$$H_s - H = T(\Phi_s - \Phi), \quad \text{or } H = T\Phi - G.$$

$$V_s - V = V_s(H_s - H)/(H_s - s) \text{ Cent.} = V_s(H_s - H)/(H_s - s(t - 82)) \text{ Fahr.}$$

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# TABLE III.—PROPERTIES OF SATURATED STEAM IN TERMS OF TEMPERATURE.

III. (p).—SATURATION PRESSURE  $p$  OF STEAM IN POUNDS PER SQ. IN. (LONDON) FOR EACH DEGREE C. FROM 0° TO 250° C.

temperature.		0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
C.	F.										
0	32	0.08922	0.09589	0.10299	0.11058	0.11862	0.12720	0.13632	0.14601	0.15631	0.16724
10	50	0.17883	0.19112	0.20415	0.21797	0.23260	0.24810	0.26449	0.28182	0.30014	0.31949
20	68	0.33993	0.36157	0.38433	0.40834	0.43366	0.46034	0.48844	0.51804	0.54915	0.58190
30	86	0.61618	0.65236	0.69037	0.73030	0.77222	0.81624	0.86234	0.91075	0.96150	1.0147
40	104	1.0703	1.1286	1.1896	1.2534	1.3202	1.3900	1.4631	1.5393	1.6187	1.7020
50	122	1.7888	1.8793	1.9738	2.0723	2.1750	2.2820	2.3935	2.5096	2.6305	2.7564
60	140	2.8873	3.0234	3.1651	3.3123	3.4653	3.6243	3.7896	3.9611	4.1392	4.3240
70	158	4.5156	4.7144	4.9205	5.1343	5.3560	5.5857	5.8236	6.0700	6.3253	6.5893
80	176	6.8627	7.1451	7.4377	7.7392	8.0525	8.3763	8.7100	9.0554	9.4122	9.7805
90	194	10.161	10.553	10.958	11.375	11.806	12.252	12.710	13.182	13.670	14.172
100	212	14.689	15.222	15.770	16.335	16.916	17.515	18.131	18.765	19.417	20.086
110	230	20.777	21.486	22.214	22.964	23.733	24.523	25.336	26.170	27.027	27.906
120	248	28.608	29.703	30.836	31.658	32.658	33.684	34.735	35.813	36.920	38.052
130	266	39.213	40.403	41.621	42.869	44.147	45.456	46.797	48.169	49.574	51.011
140	284	52.482	53.986	55.525	57.098	58.709	60.355	62.038	63.759	65.516	67.313
150	302	69.150	71.025	72.941	74.898	76.897	78.939	81.021	83.150	85.322	87.539
160	320	89.800	92.106	94.460	96.861	99.314	101.81	104.36	106.96	109.61	112.31
170	338	115.06	117.86	120.72	123.63	126.60	129.62	132.70	135.83	139.03	142.28
180	356	145.59	148.95	152.38	155.87	159.43	163.04	166.72	170.46	174.27	178.14
190	374	182.08	186.08	190.16	194.29	198.50	202.78	207.12	211.55	216.04	220.60
200	392	225.24	229.95	234.73	239.59	244.52	249.53	254.62	259.79	265.05	270.38
210	410	275.78	281.26	286.82	292.47	298.20	304.01	309.91	315.90	321.97	328.13
220	428	334.38	340.71	347.14	353.66	360.26	366.96	373.76	380.64	387.63	394.70
230	446	401.89	409.12	416.46	423.89	431.01	438.06	446.79	454.62	462.50	470.60
240	464	478.74	486.95	495.27	503.69	512.21	520.85	529.59	538.43	547.38	556.46
250	482	565.63	574.87	584.22	593.69	603.26	612.96	622.74	632.67	642.70	652.84
0		1.8	3.6	5.4	7.2	9.0	10.8	12.6	14.4	16.2	

EQUIVALENT DEGREES AND DECIMALS FAHRENHEIT.

To reduce to kg/sq. cm. (London) multiply by 0.070307.

To reduce to Latitude 45° add 1/2000th part.

To reduce to mm. of mercury (Lat. 45°) multiply by 760/14.689.

Reduction is best effected by the aid of the table of logarithms of the pressure given on the opposite page.

The values of  $p$  are calculated from the thermodynamical equation  $T\phi - h = T\phi - H$ , to be consistent with those of  $H$  and  $\phi$ . They agree very closely with experiment from 0° to 200° C. Beyond 200° C. the experimental results become less certain, but the error of the formula is certainly less than 1° C. at 250° C.

TABLE III.—PROPERTIES OF SATURATED STEAM IN TERMS OF TEMPERATURE.

III. (log p).—LOG<sub>10</sub> p FOR EACH 1° C. FROM 0° TO 250° C.

Temperature.		0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
C.	F.										
0	32	95046	98175	01280	04359	07416	10449	13456	16440	19399	22333
10	50	25244	28130	30995	33839	36661	39462	42241	44997	47733	50446
20	68	53139	55840	58471	61102	63715	66308	68884	71436	73969	76485
30	86	78971	81449	83908	86350	88774	91182	93568	95940	98295	00632
40	104	02950	05253	07539	09809	12063	14302	16527	18731	20917	23097
50	122	25256	27400	29530	31644	33745	35832	37904	39961	42004	44034
60	140	46050	48050	50039	52013	53974	55922	57859	59782	61692	63588
70	158	65472	67343	69201	71048	72884	74708	76519	78319	80108	81884
80	176	83649	85401	87144	88874	90593	92305	94002	95691	97369	99036
90	194	00692	02337	03971	05595	07212	08819	10413	11998	13576	15142
100	212	10699	18246	19783	21312	22831	24342	25843	27335	28819	30293
110	230	31759	33215	34663	36104	37535	38958	40373	41780	43179	44569
120	248	45951	47324	48690	50049	51399	52742	54077	55404	56720	58038
130	266	59343	60641	61931	63214	64490	65759	67022	68277	69525	70766
140	284	72901	73228	74449	75662	76870	78071	79266	80454	81635	82810
150	302	83979	85141	86297	87447	88591	89729	90860	91986	93106	94220
160	320	95328	96429	97525	98615	99701	00779	01853	02921	03983	05041
170	338	06092	07137	08177	09212	10242	11267	12287	13301	14310	15316
180	356	16313	17305	18294	19277	20257	21230	22199	23163	24122	25077
190	374	26027	26971	27911	28845	29775	30702	31623	32541	33453	34361
200	392	35265	36163	37056	37947	38832	39713	40590	41463	42332	43197
210	410	44057	44911	45761	46608	47450	48289	49123	49955	50782	51604
220	428	52424	53239	54050	54858	55661	56462	57259	58052	58842	59627
230	446	60410	61185	61957	62725	63490	64252	65010	65765	66517	67266
240	464	68010	68748	69484	70216	70945	71671	72394	73113	73829	74542
250	482	75253	75957	76658	77356	78050	78743	79431	80118	80800	81481
		0	1·8	3·6	5·4	7·2	9·0	10·8	12·6	14·4	16·2

EQUIVALENT DEGREES AND DECIMALS FAHRENHEIT.

$\log p = 21.07449 - 2903.39/T + 4.71784 \log T + 0.4057(c - b)p/T$ .  
 To reduce to kg/sq. cm. add  $\log 0.070307 = 2.84696$ . To reduce to mms. of mercury (Lat. 45°) add 1.71382.

The characteristic of the logarithm is omitted, and must be supplied by inspection of the table of  $\bar{p}$  on the opposite page.

The logarithm of the pressure is the quantity directly given by calculation, and most often required for other purposes. It should be used, when possible, in preference to  $p$  itself, because this procedure permits a more uniform degree of proportionate accuracy.

# TABLE III.—PROPERTIES OF SATURATED STEAM IN TERMS OF TEMPERATURE.

III. (V).—VOLUME OF SATURATED STEAM  $V_s$ , IN CUBIC FEET PER POUND FOR EACH  
1° C. FROM 0° TO 259° C.

Temperature. F.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
0 32	3275.9	3050.3	2858.5	2672.6	2499.9	2339.8	2190.9	2052.6	1924.2	1804.8
10 50	1693.8	1590.5	1494.1	1404.3	1320.4	1242.2	1169.2	1101.1	1037.3	977.87
20 68	922.19	869.92	821.13	775.45	732.59	692.41	654.84	619.36	586.18	554.98
30 86	575.81	498.25	472.33	447.94	424.99	403.33	382.98	363.77	345.64	328.56
40 104	312.45	297.24	282.87	269.28	256.45	244.30	232.81	221.96	211.69	201.93
50 122	192.72	183.97	175.05	167.84	160.37	153.30	146.58	140.20	134.15	128.38
60 140	122.91	117.72	112.76	108.06	103.58	99.307	95.238	91.364	87.673	84.156
70 158	80.804	77.006	74.558	71.644	68.894	66.204	63.660	61.244	58.926	56.713
80 176	54.596	52.573	50.633	48.781	47.007	45.303	43.677	42.115	40.620	39.187
90 194	37.815	36.498	35.235	34.024	32.860	31.743	30.670	29.642	28.651	27.702
100 212	26.789	25.911	25.067	24.256	23.476	22.724	22.001	21.306	20.636	19.992
110 230	19.370	18.774	18.197	17.641	17.105	16.590	16.092	15.612	15.149	14.702
120 248	14.271	13.855	13.454	13.066	12.692	12.330	11.980	11.643	11.316	11.001
130 266	10.696	10.401	10.116	9.8404	9.5737	9.3156	9.0654	8.8236	8.5894	8.3627
140 284	8.1431	7.9304	7.7245	7.5252	7.3317	7.1443	6.9625	6.7864	6.6158	6.4502
150 302	6.2895	6.1330	5.9828	5.8361	5.6939	5.5559	5.4218	5.2916	5.1652	5.0424
160 320	4.9232	4.8076	4.6951	4.5860	4.4795	4.3763	4.2758	4.1782	4.0835	3.9911
176 338	3.9015	3.8143	3.7295	3.6469	3.5675	3.4884	3.4123	3.3383	3.2661	3.1959
180 356	3.1275	3.0611	2.9962	2.9331	2.8714	2.8115	2.7531	2.6962	2.6408	2.5867
190 374	2.5339	2.4826	2.4324	2.3838	2.3362	2.2896	2.2444	2.2001	2.1570	2.1148
200 392	2.0738	2.0337	1.9948	1.9566	1.9193	1.8830	1.8474	1.8128	1.7788	1.7458
210 410	1.7134	1.6819	1.6511	1.6210	1.5916	1.5629	1.5348	1.5073	1.4804	1.4542
220 428	1.4285	1.4034	1.3788	1.3548	1.3314	1.3084	1.2860	1.2639	1.2424	1.2214
230 446	1.2007	1.1807	1.1611	1.1419	1.1230	1.1046	1.0864	1.0688	1.0555	1.0344
240 464	1.0178	1.0017	0.9858	0.9702	0.9549	0.9400	0.9253	0.9110	0.8969	0.8830
250 482	0.8895	0.8564	0.8434	0.8306	0.8183	0.8060	0.7940	0.7822	0.7707	0.7594
	0	1.8	3.6	5.4	7.2	9.0	10.8	12.6	14.4	16.2

EQUIVALENT DEGREES AND DECIMALS FAHRENHEIT.

Formula  $V_s = 1.070617/p - (c - b)$ .

Where  $T = t + 273.10^\circ \text{C.}$ ,  $b = 0.0160$ , and  $c = 0.4213(373.1/T)^{10/3}$ .

$p$  in lbs./sq. in. London.  $c$  and  $b$  in cubic feet per pound.

To reduce to cubic metres per kilogramme divide by 16.0184 (or divide by 16 and subtract .00115 of the result).

To find  $V$  for wet steam, given  $t$ , and  $H$  or  $\phi$ , find  $H_s$  from Table III., p. 30 (and  $E$  from  $H_s \cdot T\phi - G$ , Table III., p. 31, if  $\phi$  only is given), and substitute in the formula  $V_s - V = V_s(H_s - H)/(H_s - sf)$ .

TABLE III.—PROPERTIES OF SATURATED STEAM IN TERMS OF TEMPERATURE.

III. (c).—CO-AGGREGATION VOLUME  $c$  IN CUBIC FEET PER POUND FOR EACH  
1° C. FROM 0° TO 259° C.

Temperature.		0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
C.	F.										
0	32	1.192	1.177	1.163	1.149	1.135	1.122	1.109	1.096	1.083	1.070
10	50	1.057	1.045	1.033	1.021	1.009	0.9972	0.9857	0.9744	0.9634	0.9525
20	68	0.9417	0.9310	0.9195	0.9101	0.9001	0.8900	0.8803	0.8705	0.8609	0.8514
30	86	0.8420	0.8328	0.8237	0.8147	0.8060	0.7973	0.7888	0.7804	0.7720	0.7638
40	104	0.7557	0.7477	0.7397	0.7320	0.7243	0.7168	0.7094	0.7020	0.6947	0.6875
50	122	0.6804	0.6734	0.6665	0.6597	0.6530	0.6465	0.6400	0.6336	0.6272	0.6209
60	140	0.6147	0.6086	0.6025	0.5966	0.5907	0.5850	0.5793	0.5736	0.5680	0.5625
70	158	0.5570	0.5516	0.5463	0.5410	0.5358	0.5307	0.5258	0.5208	0.5158	0.5109
80	176	0.5061	0.5013	0.4966	0.4920	0.4874	0.4829	0.4785	0.4741	0.4697	0.4654
90	194	0.4611	0.4569	0.4527	0.4486	0.4445	0.4404	0.4366	0.4327	0.4288	0.4250
100	212	0.4213	0.4174	0.4137	0.4101	0.4064	0.4029	0.3995	0.3960	0.3925	0.3891
110	230	0.3857	0.3823	0.3790	0.3758	0.3726	0.3694	0.3663	0.3632	0.3601	0.3570
120	248	0.3540	0.3510	0.3480	0.3451	0.3422	0.3393	0.3365	0.3337	0.3310	0.3282
130	266	0.3255	0.3228	0.3202	0.3175	0.3149	0.3123	0.3098	0.3073	0.3049	0.3024
140	284	0.3000	0.2976	0.2952	0.2929	0.2905	0.2882	0.2860	0.2837	0.2815	0.2793
150	302	0.2771	0.2749	0.2727	0.2706	0.2684	0.2663	0.2643	0.2622	0.2602	0.2582
160	320	0.2562	0.2542	0.2523	0.2503	0.2484	0.2466	0.2448	0.2430	0.2411	0.2393
170	338	0.2375	0.2357	0.2340	0.2322	0.2305	0.2287	0.2270	0.2253	0.2237	0.2220
180	356	0.2204	0.2188	0.2172	0.2156	0.2141	0.2126	0.2110	0.2095	0.2080	0.2065
190	374	0.2050	0.2035	0.2021	0.2006	0.1992	0.1978	0.1964	0.1950	0.1936	0.1923
200	392	0.1909	0.1896	0.1882	0.1869	0.1856	0.1843	0.1830	0.1817	0.1805	0.1792
210	410	0.1780	0.1768	0.1756	0.1744	0.1732	0.1720	0.1709	0.1697	0.1686	0.1674
220	428	0.1663	0.1652	0.1641	0.1630	0.1619	0.1608	0.1597	0.1587	0.1576	0.1565
230	446	0.1555	0.1545	0.1534	0.1524	0.1514	0.1504	0.1495	0.1485	0.1475	0.1466
240	464	0.1456	0.1446	0.1437	0.1428	0.1419	0.1410	0.1401	0.1392	0.1383	0.1375
250	482	0.1366	0.1357	0.1349	0.1341	0.1332	0.1324	0.1316	0.1308	0.1300	0.1292
		0	1.8	3.6	5.4	7.2	9.0	10.8	12.6	14.4	16.2

EQUIVALENT DEGREES AND DECIMALS FAHRENHEIT.

$$\text{Formula } c = 0.4218(373.1/T)^{10.3}.$$

Where  $T = 273.10 + t$ , Centigrade.

To reduce to cubic metres per kilo divide by 16.0184. (Divide by 16 and subtract 0.00115 of the result.)

Since  $c$  is a function of the temperature only, the values given in this table apply to dry steam, whether superheated or supersaturated, as well as to dry saturated steam. The relative values are correct to about 1 in 2000, but the absolute values are uncertain to about 1 per cent.



# TABLE III.—PROPERTIES OF SATURATED STEAM IN TERMS OF TEMPERATURE

II. (H).—TOTAL HEAT  $H_s$  OF SATURATED STEAM IN MEAN CALORIES C. FROM 0° TO 259° C. FOR EACH DEGREE.

Temperature. ° F.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
0	32	594.27	594.75	595.23	595.70	596.18	596.65	597.13	597.60	598.07
10	50	599.01	599.49	599.96	600.43	600.90	601.37	601.84	602.31	602.78
20	68	603.72	604.19	604.66	605.13	605.60	606.06	606.53	607.00	607.47
30	86	608.40	608.87	609.33	609.80	610.26	610.73	611.19	611.65	612.12
40	104	613.04	613.50	613.96	614.42	614.88	615.34	615.80	616.26	616.72
50	122	617.63	618.09	618.54	619.00	619.45	619.90	620.36	620.81	621.26
60	140	622.16	622.61	623.06	623.50	623.95	624.39	624.84	625.28	625.72
70	158	626.60	627.04	627.48	627.91	628.35	628.79	629.22	629.65	630.09
80	176	630.95	631.38	631.80	632.23	632.65	633.08	633.50	633.93	634.35
90	194	635.19	635.61	636.02	636.44	636.85	637.26	637.67	638.08	638.49
100	212	639.30	639.71	640.11	640.51	640.90	641.30	641.69	642.09	642.48
110	230	643.20	643.60	644.00	644.42	644.80	645.18	645.56	645.94	646.32
120	248	647.07	647.46	647.84	648.22	648.59	648.96	649.33	649.70	650.07
130	266	650.72	651.09	651.46	651.83	652.19	652.56	652.92	653.29	653.65
140	284	654.19	654.55	654.91	655.27	655.63	655.99	656.35	656.71	657.07
150	302	657.47	657.82	658.18	658.54	658.90	659.26	659.62	659.98	660.34
160	320	660.55	660.90	661.25	661.61	661.96	662.32	662.67	663.03	663.38
170	338	663.44	663.79	664.14	664.49	664.84	665.19	665.54	665.89	666.24
180	356	666.14	666.49	666.84	667.19	667.54	667.89	668.24	668.59	668.94
190	374	668.65	668.99	669.34	669.69	670.04	670.39	670.74	671.09	671.44
200	392	670.06	670.40	670.75	671.10	671.45	671.80	672.15	672.50	672.85
210	410	673.09	673.43	673.78	674.13	674.48	674.83	675.18	675.53	675.88
220	428	675.06	675.40	675.75	676.10	676.45	676.80	677.15	677.50	677.85
230	446	676.87	677.21	677.56	677.91	678.26	678.61	678.96	679.31	679.66
240	464	678.55	678.89	679.24	679.59	679.94	680.29	680.64	680.99	681.34
250	482	680.12	680.46	680.81	681.16	681.51	681.86	682.21	682.56	682.91
		0	1.8	3.6	5.4	7.2	9.0	10.8	12.6	14.4

EQUIVALENT DEGREES AND DECIMALS FAHRENHEIT.

Equation  $H_s = S_0 T - (a(n+1)c - ab)p + 464.00$ .

Where  $S_0 = (n+1)R = 13 \times 0.11012/3$ , and  $p$  = saturation pressure in lbs. per sq. in.

$a = 144/1400$ .  $c = 0.4213/(T/878.1)^{10/3}$ .  $b = 0.0160$ .

To reduce to British Thermal Units, multiply by 9/5. (Subtract a tenth and multiply by 2.)

No reduction required for Metric Units C.

To find  $H$  for wet steam, given  $\phi$  and  $t$ .  $H = T\phi - G$ .

To find  $H$  for wet steam, given  $V$  and  $t$ . Find  $V_s$  from Table III. (V) p. 28, and substitute in the formula,  $V_s - V = V_s(H_s - H)/(H_s - sf)$ .

When  $\phi$  and  $V$  are given, proceed by trial and interpolation.

TABLE III.—PROPERTIES OF SATURATED STEAM IN TERMS OF TEMPERATURE.

III. (G).—THERMODYNAMIC POTENTIAL  $G_s = T\phi_s - H_s$  OF SATURATED STEAM IN MEAN CALORIES C. FOR EACH 1° FROM 0° TO 250° C.

Temperature.		0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
C.	F.										
0	32	0	0.002	0.007	0.016	0.029	0.046	0.066	0.090	0.116	0.146
10	50	0.181	0.218	0.259	0.304	0.352	0.405	0.459	0.517	0.579	0.645
20	68	0.714	0.79	0.86	0.93	1.01	1.10	1.19	1.28	1.38	1.48
30	86	1.58	1.69	1.79	1.90	2.02	2.14	2.26	2.39	2.51	2.64
40	104	2.78	2.92	3.06	3.20	3.35	3.50	3.65	3.81	3.97	4.13
50	122	4.30	4.47	4.64	4.82	4.99	5.17	5.36	5.55	5.74	5.93
60	140	6.13	6.33	6.53	6.74	6.95	7.16	7.37	7.59	7.81	8.03
70	158	8.26	8.49	8.72	8.96	9.20	9.44	9.68	9.93	10.17	10.43
80	176	10.68	10.94	11.20	11.46	11.73	12.00	12.27	12.54	12.82	13.10
90	194	13.38	13.67	13.96	14.25	14.54	14.84	15.13	15.43	15.74	16.05
100	212	16.36	16.67	16.99	17.31	17.63	17.95	18.27	18.60	18.93	19.26
110	230	19.60	19.94	20.28	20.62	20.97	21.32	21.67	22.02	22.38	22.74
120	248	23.10	23.46	23.83	24.20	24.57	24.95	25.33	25.71	26.09	26.47
130	266	26.80	27.25	27.61	28.04	28.41	28.81	29.24	29.64	30.04	30.45
140	284	30.80	31.27	31.68	32.10	32.52	32.94	33.37	33.80	34.23	34.66
150	302	35.10	35.54	35.98	36.42	36.86	37.31	37.76	38.21	38.66	39.12
160	320	39.58	40.04	40.50	40.97	41.44	41.91	42.38	42.85	43.33	43.81
170	338	44.29	44.77	45.25	45.74	46.23	46.72	47.22	47.72	48.22	48.72
180	356	49.22	49.73	50.24	50.75	51.26	51.77	52.29	52.81	53.33	53.85
190	374	54.38	54.91	55.44	55.97	56.50	57.04	57.58	58.12	58.66	59.20
200	392	59.75	60.30	60.85	61.40	61.96	62.52	63.08	63.64	64.20	64.76
210	410	65.33	65.90	66.47	67.04	67.62	68.20	68.78	69.36	69.94	70.53
220	428	71.12	71.71	72.30	72.89	73.49	74.09	74.69	75.29	75.89	76.50
230	446	77.11	77.72	78.33	78.94	79.56	80.18	80.80	81.42	82.04	82.67
240	464	83.30	83.93	84.56	85.19	85.82	86.46	87.10	87.74	88.38	89.03
250	482	89.68	90.33	90.98	91.63	92.28	92.94	93.60	94.26	94.92	95.59
		0	1.8	3.6	5.4	7.2	9.0	10.8	12.6	14.4	16.2

EQUIVALENT DEGREES AND DECIMALS FAHRENHEIT.

$$\text{Equation } G_s = sT \log_e T/T_0 - st - 0.003 t/T_0$$

$$= 2.2949 T \log_{10} T/273.1 - t + t/300 - 0.003 t/273.1$$

where  $s = 0.99666$ , and  $T = t + 273.10$ .

To reduce  $G$  to British Thermal Units, multiply by 9/5, or subtract a tenth and multiply by 2.

No reduction required for Metric Units Centigrade.

The value of  $G$  is the same for water and saturated steam at the same temperature or pressure, and for a mixture of water and steam in any proportions.

**TABLE IV.—TOTAL HEAT  $H$  OF SUPERHEATED OR SUPERSATURATED STEAM  
IN MEAN CALORIES CENTIGRADE.**

Temperature.		Difference for 10 lbs. 10 S.C.	Pressure in pounds per sq. in. (Kg. per sq. cm. in <i>italics</i> .)									
			20	30	40	50	60	70	80	90	100	
			1:4061	2:1093	2:8123	3:5154	4:2184	4:9215	5:6246	6:3278	7:0307	
500	932	0.1492	832.61	832.46	832.31	832.16	832.02	831.87	831.72	831.57	831.42	
450	842	0.1904	808.67	808.48	808.29	808.10	807.91	807.72	807.53	807.34	807.15	
400	752	0.2404	784.70	784.45	784.20	783.96	783.71	783.47	783.22	782.97	782.73	
390	734	0.2596	779.90	779.64	779.38	779.12	778.86	778.60	778.34	778.08	777.82	
380	716	0.2740	775.10	774.82	774.55	774.28	774.00	773.73	773.45	773.18	772.91	
370	698	0.2892	770.30	770.01	769.72	769.43	769.14	768.85	768.56	768.27	767.98	
360	680	0.3056	765.49	765.19	764.88	764.57	764.27	763.96	763.66	763.35	763.05	
350	662	0.3232	760.68	760.36	760.04	759.71	759.39	759.07	758.74	758.42	758.10	
340	644	0.3420	755.87	755.53	755.19	754.85	754.51	754.16	753.82	753.48	753.14	
330	626	0.3620	751.06	750.70	750.34	749.98	749.61	749.25	748.89	748.53	748.17	
320	608	0.3840	746.25	745.86	745.48	745.09	744.71	744.33	743.94	743.56	743.17	
310	590	0.4072	741.43	741.02	740.61	740.21	739.80	739.39	738.98	738.58	738.17	
300	572	0.4324	736.61	736.17	735.74	735.31	734.88	734.44	734.01	733.58	733.15	
290	554	0.4596	731.78	731.32	730.86	730.40	729.94	729.48	729.02	728.56	728.10	
280	536	0.4888	726.95	726.46	725.97	725.48	724.99	724.50	724.02	723.53	723.04	
270	518	0.5204	722.14	721.59	721.07	720.55	720.03	719.51	718.99	718.47	717.95	
260	500	0.5544	717.27	716.72	716.16	715.61	715.06	714.50	713.95	713.39	712.84	
250	482	0.5920	712.43	711.83	711.24	710.65	710.06	709.47	708.87	708.28	707.69	
240	464	0.6324	707.57	706.94	706.31	705.68	705.04	704.41	703.78	703.15	702.51	
230	446	0.6764	702.71	702.04	701.36	700.69	700.01	699.33	698.66	697.98	697.30	
220	428	0.7244	697.85	697.12	696.40	695.67	694.95	694.23	693.50	692.78	692.05	
210	410	0.7768	692.97	692.19	691.42	690.64	689.86	689.09	688.31	687.53	686.76	
200	392	0.8340	688.08	687.25	686.42	685.58	684.75	683.91	683.08	682.25	681.41	
190	374	0.8968	683.19	682.29	681.39	680.50	679.60	678.70	677.81	676.91	676.01	
180	356	0.9656	678.28	677.31	676.35	675.38	674.41	673.45	672.48	671.52	670.55	
170	338	1.0422	673.35	672.31	671.27	670.23	669.19	668.15	667.10	666.06	665.02	
160	320	1.1256	668.41	667.29	666.16	665.04	663.91	662.79	661.66	660.54	659.41	
150	302	1.2187	663.46	662.24	661.02	659.80	658.59	657.37	656.15	654.93	653.71	
140	284	1.3208	658.48	657.16	655.84	654.52	653.20	651.88	650.56	649.24	647.92	
130	266	1.4345	653.48	652.05	650.61	649.18	647.75	646.31	644.88	643.44	642.01	
120	248	1.5615	648.46	646.90	645.34	643.77	642.21	640.65	639.09	637.53	635.97	
110	230	1.7027	643.40	641.70	640.00	638.30	636.59	634.89	633.19	631.49	629.79	
100	212	1.8608	638.31	636.45	634.59	632.73	630.87	629.01	627.15	625.29	623.43	
At saturation temperature.		H.	642.82	647.53	650.95	653.60	655.76	657.60	659.20	660.69	661.82	
		C.	108.87	121.28	130.67	138.30	144.79	150.46	155.52	160.09	164.28	
		F.	227.97	250.31	267.21	280.94	292.62	302.83	311.93	320.16	327.71	

Formula  $H = S_0T - SCP + 464.00$ .  $S_0 = 0.47719$ .

To reduce to B-Th.U. Fahr., subtract a tenth and multiply by 2.

No reduction required for Metric Units (K.M.C.).

Values below the black zigzag line represent supersaturated steam.

**TABLE IV.—TOTAL HEAT  $H$  OF SUPERHEATED OR SUPER-SATURATED STEAM  
IN MEAN CALORIES CENTIGRADE.**

Pressure in pounds per square inch. (Kg. per sq. cm. in Italics.)										
120 <i>8.488</i>	140 <i>9.489</i>	160 <i>11.249</i>	180 <i>13.655</i>	200 <i>15.661</i>	250 <i>17.577</i>	300 <i>21.092</i>	350 <i>24.907</i>	400 <i>28.123</i>	450 <i>31.638</i>	500 <i>35.154</i>
831.12	830.82	830.52	830.22	829.93	829.18	828.43	827.69	826.94	826.20	825.45
806.77	806.39	806.00	805.62	805.24	804.29	803.34	802.39	801.43	800.48	799.53
782.23	781.74	781.25	780.76	780.26	779.03	777.80	776.57	775.33	774.10	772.87
777.30	776.78	776.26	775.75	775.23	773.93	772.63	771.33	770.03	768.74	767.44
772.36	771.81	771.26	770.71	770.17	768.80	767.43	766.06	764.69	763.32	761.95
767.40	766.83	766.25	765.67	765.09	763.64	762.20	760.75	759.31	757.86	756.41
762.44	761.82	761.21	760.60	759.99	758.46	756.93	755.41	753.88	752.35	750.82
757.45	756.81	756.16	755.51	754.87	753.25	751.63	750.02	748.40	746.79	745.17
752.45	751.77	751.09	750.40	749.72	748.01	746.30	744.59	742.88	741.17	739.46
747.44	746.72	745.99	745.27	744.55	742.74	740.93	739.12	737.31	735.50	733.69
742.41	741.64	740.87	740.10	739.33	737.41	735.49	733.57	731.65	729.73	727.81
737.36	736.54	735.73	734.91	734.10	732.06	730.03	727.99	725.95	723.92	721.88
732.28	731.42	730.55	729.69	728.82	726.66	724.50	722.34	720.17	718.01	715.85
727.18	726.26	725.34	724.43	723.51	721.21	718.91	716.61	714.31	712.02	709.72
722.06	721.08	720.11	719.13	718.15	715.71	713.26	710.82	708.37	705.93	703.49
716.91	715.87	714.83	713.79	712.75	710.14	707.54	704.94	702.34	699.74	697.13
711.73	710.62	709.51	708.40	707.29	704.52	701.75	698.98	696.21	693.43	690.66
706.51	705.32	704.14	702.95	701.77	698.81	695.85	692.89	689.93	686.97	684.01
701.25	699.99	698.72	697.46	696.19	693.03	689.87	686.70	683.54	680.38	677.22
695.95	694.60	693.24	691.89	690.54	687.16	683.77	680.39	677.01	673.63	670.25
690.60	689.16	687.71	686.26	684.81	681.19	677.56	673.94	670.32	666.70	663.08
685.20	683.65	682.10	680.54	678.99	675.10	671.22	667.34	663.45	659.57	655.68
679.74	678.08	676.41	674.74	673.07	668.90	664.73	660.56	656.39	652.22	648.05
674.22	672.43	670.63	668.84	667.04	662.50	658.08	653.59	649.11	644.62	640.14
668.62	666.69	664.76	662.83	660.90	656.97	651.24	646.41	641.58	636.76	631.93
662.94	660.85	658.77	656.69	654.60	649.48	644.19	638.98	633.77	628.56	623.36
657.16	654.91	652.66	650.41	648.16	642.53	636.91	631.28	625.66	620.03	614.40
651.28	648.84	646.41	643.97	641.53	635.44	629.35	623.26	617.17	611.08	604.99
645.28	642.64	640.00	637.36	634.72	628.12	621.52	614.92	608.32	601.72	595.12
639.14	636.27	633.41	630.54	627.67	620.50	613.33	606.16	598.99	591.82	584.65
632.85	629.73	626.61	623.48	620.36	612.56	604.75	596.95	589.15	581.34	573.54
626.38	622.98	619.57	616.17	612.77	604.26	595.75	587.24	578.73	570.22	561.71
619.74	615.99	612.27	608.55	604.83	595.52	586.22	576.92	567.62	558.32	549.01
613.02	608.89	604.76	600.63	596.50	586.80	577.10	567.40	557.70	548.00	538.30
606.16	601.66	597.16	592.66	588.16	578.16	568.16	558.16	548.16	538.16	528.16
600.00	595.00	590.00	585.00	580.00	570.00	560.00	550.00	540.00	530.00	520.00
593.84	588.84	583.84	578.84	573.84	563.84	553.84	543.84	533.84	523.84	513.84
587.68	582.68	577.68	572.68	567.68	557.68	547.68	537.68	527.68	517.68	507.68
581.52	576.52	571.52	566.52	561.52	551.52	541.52	531.52	521.52	511.52	501.52
575.36	570.36	565.36	560.36	555.36	545.36	535.36	525.36	515.36	505.36	495.36
569.20	564.20	559.20	554.20	549.20	539.20	529.20	519.20	509.20	499.20	489.20
563.04	558.04	553.04	548.04	543.04	533.04	523.04	513.04	503.04	493.04	483.04
556.88	551.88	546.88	541.88	536.88	526.88	516.88	506.88	496.88	486.88	476.88
550.72	545.72	540.72	535.72	530.72	520.72	510.72	500.72	490.72	480.72	470.72
544.56	539.56	534.56	529.56	524.56	514.56	504.56	494.56	484.56	474.56	464.56
538.40	533.40	528.40	523.40	518.40	508.40	498.40	488.40	478.40	468.40	458.40
532.24	527.24	522.24	517.24	512.24	502.24	492.24	482.24	472.24	462.24	452.24
526.08	521.08	516.08	511.08	506.08	496.08	486.08	476.08	466.08	456.08	446.08
519.92	514.92	509.92	504.92	499.92	489.92	479.92	469.92	459.92	449.92	439.92
513.76	508.76	503.76	498.76	493.76	483.76	473.76	463.76	453.76	443.76	433.76
507.60	502.60	497.60	492.60	487.60	477.60	467.60	457.60	447.60	437.60	427.60
501.44	496.44	491.44	486.44	481.44	471.44	461.44	451.44	441.44	431.44	421.44
495.28	490.28	485.28	480.28	475.28	465.28	455.28	445.28	435.28	425.28	415.28
489.12	484.12	479.12	474.12	469.12	459.12	449.12	439.12	429.12	419.12	409.12
482.96	477.96	472.96	467.96	462.96	452.96	442.96	432.96	422.96	412.96	402.96
476.80	471.80	466.80	461.80	456.80	446.80	436.80	426.80	416.80	406.80	396.80
470.64	465.64	460.64	455.64	450.64	440.64	430.64	420.64	410.64	400.64	390.64
464.48	459.48	454.48	449.48	444.48	434.48	424.48	414.48	404.48	394.48	384.48
458.32	453.32	448.32	443.32	438.32	428.32	418.32	408.32	398.32	388.32	378.32
452.16	447.16	442.16	437.16	432.16	422.16	412.16	402.16	392.16	382.16	372.16
446.00	441.00	436.00	431.00	426.00	416.00	406.00	396.00	386.00	376.00	366.00
439.84	434.84	429.84	424.84	419.84	409.84	399.84	389.84	379.84	369.84	359.84
433.68	428.68	423.68	418.68	413.68	403.68	393.68	383.68	373.68	363.68	353.68
427.52	422.52	417.52	412.52	407.52	397.52	387.52	377.52	367.52	357.52	347.52
421.36	416.36	411.36	406.36	401.36	391.36	381.36	371.36	361.36	351.36	341.36
415.20	410.20	405.20	400.20	395.20	385.20	375.20	365.20	355.20	345.20	335.20
409.04	404.04	399.04	394.04	389.04	379.04	369.04	359.04	349.04	339.04	329.04
402.88	397.88	392.88	387.88	382.88	372.88	362.88	352.88	342.88	332.88	322.88
396.72	391.72	386.72	381.72	376.72	366.72	356.72	346.72	336.72	326.72	316.72
390.56	385.56	380.56	375.56	370.56	360.56	350.56	340.56	330.56	320.56	310.56
384.40	379.40	374.40	369.40	364.40	354.40	344.40	334.40	324.40	314.40	304.40
378.24	373.24	368.24	363.24	358.24	348.24	338.24	328.24	318.24	308.24	298.24
372.08	367.08	362.08	357.08	352.08	342.08	332.08	322.08	312.08	302.08	292.08
365.92	360.92	355.92	350.92	345.92	335.92	325.92	315.92	305.92	295.92	285.92
359.76	354.76	349.76	344.76	339.76	329.76	319.76	309.76	299.76	289.76	279.76
353.60	348.60	343.60	338.60	333.60	323.60	313.60	303.60	293.60	283.60	273.60
347.44	342.44	337.44	332.44	327.44	317.44	307.44	297.44	287.44	277.44	267.44
341.28	336.28	331.28	326.28	321.28	311.28	301.28	291.28	281.28	271.28	261.28
335.12	330.12	325.12	320.12	315.12	305.12	295.12	285.12	275.12	265.12	255.12
328.96	323.96	318.96	313.96	308.96	298.96	288.96	278.96	268.96	258.96	248.96
322.80	317.80	312.80	307.80	302.80	292.80	282.80	272.80	262.80	252.80	242.80
316.64	311.64	306.64	301.64	296.64	286.64	276.64	266.64	256.64	246.64	236.64
310.48	305.48	300.48	295.48	290.48	280.48	270.48	260.48	250.48	240.48	230.48
304.32	299.32	294.32	289.32	284.32	274.32	264.32	254.32	244.32	234.32	224.32
298.16	293.16	288.16	283.16	278.16	268.16	258.16	248.16	238.16	228.16	218.16
292.00	287.00	282.00	277.00	272.00	262.00	252.00	242.00	232.00	222.00	212.00
285.84	280.84	275.84	270.84	265.84	255.84	245.84	235.84	225.84	215.84	205.84
279.68	274.68	269.68	264.68	259.68	249.68	239.68	229.68	219.68	209.68	199.68
273.52	268.52	263.52	258.52	253.52	243.52	233.52	223.52	213.52	203.52	193.52
267.36	262.36	257.36	252.36	247.36	237.36	227.36	217.36	207.36	197.36	187.36
261.20	256.20	251.20	246.20	241.20	231.20	221.20	211.20	201.20	191.20	181.20
255.04	250.04	245.04	240.04	235.04	225.04	215.04	205.04	195.04	185.04	175.04
248.88	243.88	238.88	233.88	228.88	218.88	208.88	198.88	188.88	178.88	168.88
242.72	237.72	232.72	227.72	222.72	212.72	202.72	192.72	182.72	172.72	162.72
236.56	231.56	226.56	221.56	216.56	206.56	196.56	186.56			

**TABLE V.—VOLUME V OF SUPERHEATED OR SUPERSATURATED STEAM  
IN CUBIC FEET PER POUND.**

Temperature.		Pressure in pounds per sq. in. (Kg. per sq. cm. in italics.)								
C.	F.	20 (1.4061)	30 2.1092	40 2.6123	50 3.5154	60 4.2184	70 4.9215	80 5.6246	90 6.3276	100 7.0307
600	932	41.363	27.349	20.671	16.532	13.774	11.803	10.325	9.1754	8.2558
450	842	38.678	25.775	19.324	15.453	12.872	11.029	9.6466	8.5714	7.7111
400	752	35.988	23.978	17.973	14.370	11.967	10.252	8.9648	7.9040	7.1632
390	764	35.450	23.618	17.702	14.152	11.786	10.096	8.8281	7.8421	7.0533
380	716	34.912	23.258	17.431	13.935	11.604	9.9396	8.6910	7.7200	6.9430
370	698	34.372	22.897	17.160	13.717	11.422	9.7833	8.5537	7.5975	6.8325
360	680	33.834	22.537	16.889	13.500	11.240	9.6266	8.4162	7.4748	6.7217
350	662	33.295	22.177	16.617	13.282	11.058	9.4698	8.2785	7.3520	6.6107
340	644	32.755	21.815	16.345	13.063	10.875	9.3125	8.1403	7.2287	6.4994
330	626	32.215	21.454	16.073	12.845	10.692	9.1551	8.0020	7.1052	6.3878
320	608	31.675	21.092	15.800	12.626	10.509	8.9973	7.8634	6.9815	6.2760
310	590	31.135	20.730	15.528	12.406	10.326	8.8391	7.7243	6.8572	6.1636
300	572	30.594	20.368	15.254	12.187	10.141	8.6805	7.5848	6.7327	6.0509
290	554	30.052	20.004	14.984	11.966	9.9569	8.5215	7.4449	6.6076	5.9378
280	536	29.510	19.641	14.706	11.746	9.7718	8.3620	7.3045	6.4821	5.8241
270	518	28.967	19.277	14.431	11.524	9.5863	8.2019	7.1636	6.3560	5.7100
260	500	28.425	18.913	14.156	11.303	9.4002	8.0413	7.0221	6.2295	5.5953
250	482	27.881	18.547	13.880	11.080	9.2134	7.8800	6.8799	6.1021	5.4798
240	464	27.337	18.181	13.603	10.857	9.0260	7.7180	6.7370	5.9741	5.3637
230	446	26.791	17.814	13.326	10.632	8.8376	7.5551	6.5933	5.8452	5.2467
220	428	26.246	17.447	13.048	10.408	8.6483	7.3913	6.4486	5.7155	5.1289
210	410	25.699	17.078	12.768	10.182	8.4582	7.2267	6.3031	5.5848	5.0101
200	392	25.150	16.709	12.488	9.9552	8.2668	7.0609	6.1564	5.4529	4.8901
190	374	24.601	16.338	12.206	9.7269	8.0743	6.8938	6.0085	5.3199	4.7690
180	356	24.050	15.965	11.923	9.4974	7.8805	6.7255	5.8592	5.1855	4.6465
170	338	23.497	15.591	11.638	9.2661	7.6850	6.5555	5.7083	5.0495	4.5244
160	320	22.944	15.216	11.352	9.0334	7.4878	6.3838	5.5558	4.9118	4.3966
150	302	22.388	14.838	11.063	8.7984	7.2886	6.2101	5.4012	4.7721	4.2687
140	284	21.829	14.458	10.773	8.5613	7.0871	6.0341	5.2443	4.6301	4.1386
130	266	21.268	14.075	10.479	8.3217	6.8832	5.8557	5.0860	4.4856	4.0061
120	248	20.705	13.691	10.183	8.0791	6.6762	5.6742	4.9227	4.3382	3.8706
110	230	20.138	13.302	9.8840	7.8332	6.4661	5.4896	4.7572	4.1875	3.7318
100	212	19.567	12.910	9.5809	7.5837	6.2522	5.3001	4.5878	4.0331	3.5892
Saturation Temperature	C.	108.87	121.28	130.67	138.30	144.70	150.46	155.52	160.09	164.28
	F.	227.97	250.31	267.21	280.94	292.62	302.83	311.93	320.16	327.71

To reduce to cubic metres per kilogram divide by 16.0184 (divide by 16 and subtract 0.00115 of the result).

No reduction required for F.P.F. units.

**TABLE V.—VOLUME V OF SUPERHEATED OR SUPERSATURATED STEAM  
IN CUBIC FEET PER POUND.**

Pressure in pounds per sq. in. (Kg. per sq. cm. in italics.)										
120	140	160	180	200	250	300	350	400	450	500
<i>84363</i>	<i>94330</i>	<i>11249</i>	<i>12555</i>	<i>14061</i>	<i>17057</i>	<i>21093</i>	<i>24607</i>	<i>28125</i>	<i>31638</i>	<i>35154</i>
6.6763	5.8910	5.1520	4.5772	4.1173	3.2897	2.7379	2.3437	2.0481	1.8182	1.6342
6.4209	5.4993	4.8081	4.2705	3.8404	3.0662	2.5501	2.1815	1.9050	1.6900	1.5179
6.0009	5.1043	4.4609	3.9605	3.6001	2.8395	2.3591	2.0159	1.7586	1.5584	1.3983
5.8701	5.0250	4.3911	3.8982	3.5037	2.7937	2.3205	1.9825	1.7289	1.5317	1.3739
5.7776	4.9452	4.3209	3.8353	3.4469	2.7477	2.2815	1.9486	1.6988	1.5046	1.3492
5.6850	4.8653	4.2506	3.7725	3.3899	2.7014	2.2424	1.9146	1.6687	1.4774	1.3244
5.5921	4.7852	4.1800	3.7093	3.3327	2.6549	2.2030	1.8803	1.6382	1.4499	1.2993
5.4989	4.7048	4.1091	3.6459	3.2753	2.6081	2.1635	1.8458	1.6075	1.4222	1.2740
5.4054	4.6240	4.0379	3.5821	3.2175	2.5611	2.1235	1.8109	1.5765	1.3941	1.2483
5.3117	4.5430	3.9665	3.5182	3.1594	2.5137	2.0833	1.7758	1.5452	1.3659	1.2224
5.2177	4.4618	3.8948	3.4530	3.1011	2.4661	2.0428	1.7404	1.5136	1.3375	1.1962
5.1232	4.3800	3.8226	3.3891	3.0423	2.4179	2.0018	1.7046	1.4816	1.3082	1.1694
5.0284	4.2980	3.7501	3.3240	2.9831	2.3696	1.9605	1.6683	1.4462	1.2788	1.1424
4.9330	4.2153	3.6771	3.2585	2.9235	2.3206	1.9187	1.6317	1.4164	1.2480	1.1149
4.8372	4.1323	3.6036	3.1924	2.8634	2.2712	1.8765	1.5945	1.3830	1.2185	1.0860
4.7409	4.0487	3.5295	3.1258	2.8027	2.2212	1.8337	1.5568	1.3491	1.1876	1.0584
4.6441	3.9646	3.4550	3.0587	2.7416	2.1709	1.7894	1.5186	1.3148	1.1562	1.0294
4.5465	3.8798	3.3797	2.9908	2.6797	2.1196	1.7463	1.4796	1.2796	1.1240	0.9996
4.4481	3.7942	3.3037	2.9222	2.6171	2.0677	1.7015	1.4399	1.2437	1.0911	0.9691
4.3490	3.7078	3.2269	2.8529	2.5536	2.0149	1.6559	1.3994	1.2071	1.0574	0.9377
4.2490	3.6205	3.1492	2.7826	2.4893	1.9614	1.6094	1.3580	1.1695	1.0209	0.9055
4.1481	3.5324	3.0706	2.7114	2.4241	1.9068	1.5620	1.3158	1.1310	0.9874	0.8724
4.0459	3.4430	2.9908	2.6390	2.3576	1.8511	1.5135	1.2723	1.0914	0.9507	0.8381
3.9427	3.3524	2.9097	2.5655	2.2900	1.7941	1.4637	1.2276	1.0505	0.9128	0.8026
3.8380	3.2606	2.8274	2.4906	2.2210	1.7360	1.4126	1.1816	1.0083	0.8736	0.7658
3.7317	3.1670	2.7434	2.4140	2.1504	1.6760	1.3598	1.1339	0.9645	0.8327	0.7273
3.6238	3.0718	2.6578	2.3358	2.0782	1.6145	1.3054	1.0816	0.9190	0.7902	0.6872
3.5138	2.9745	2.5701	2.2555	2.0039	1.5508	1.2480	1.0332	0.8714	0.7456	0.6449
3.4016	2.8751	2.4802	2.1731	1.9273	1.4851	1.1902	0.9796	0.8217	0.6984	0.6005
3.2869	2.7731	2.3878	2.0881	1.8483	1.4167	1.1296	0.9235	0.7694	0.6495	0.5536
3.1791	2.6681	2.2924	2.0001	1.7663	1.3454	1.0649	0.8615	0.7141	0.5972	0.5037
3.0482	2.5599	2.1937	1.9089	1.6810	1.2708	0.9975	0.8022	0.6557	0.5417	0.4506
2.9235	2.4480	2.0913	1.8140	1.5920	1.1926	0.9263	0.7461	0.5934	0.4826	0.3927
171.75	178.31	184.16	189.48	194.36	205.10	214.32	222.45	229.75	236.42	242.57
341.15	352.96	363.49	373.07	381.85	401.19	417.78	432.41	445.55	457.56	468.63

Values below the black zigzag line represent supersaturated steam.

Formula  $V = 1.07061T/P - 0.4213(T_1/T)^{10/3} + 0.0160$ ,  
where  $T = 273.10 + t$  Cent., and  $T_1 = 373.10^\circ$ .

**TABLE VI.—ENTROPY  $\phi$  OF SUPERHEATED OR SUPERSATURATED STEAM  
IN THERMAL UNITS PER DEGREE, CENTIGRADE OR FAHRENHEIT.**

Temperature.		Pressure in pounds per sq. in. (Kg. per sq. cm. in italics.)									
		20	30	40	50	60	70	80	90	100	
C.	F.	1.4061	2.1008	2.8123	3.5164	4.2184	4.9215	5.6246	6.3276	7.0307	
500	932	07640	08158	99974	97500	95465	93762	92274	90960	89781	
450	842	04439	99052	96762	94283	92252	90534	89040	87721	86541	
400	752	01003	96508	93370	90823	88784	87068	85566	84229	83041	
390	724	00284	95787	92587	90098	88057	86320	84825	83496	82301	
380	716	99555	95056	91853	89362	87319	85589	84082	82751	81556	
370	698	98813	94310	91107	88613	86567	84835	83326	81993	80797	
360	680	98061	93557	90350	87853	85805	84071	82559	81223	80025	
350	662	97294	92787	89577	87078	85028	83290	81776	80437	79236	
340	644	96516	92005	88792	86290	84236	82495	80978	79636	78432	
330	626	95724	91211	87995	85489	83432	81688	80168	78822	77615	
320	608	94919	90402	87182	84673	82613	80865	79341	77992	76781	
310	590	94099	89578	86354	83841	81777	80025	78497	77144	75929	
300	572	93264	88739	85511	82993	80924	79168	77636	76278	75059	
290	554	92416	87886	84653	82134	80057	78296	76759	75397	74173	
280	536	91551	87016	83778	81250	79171	77405	75863	74495	73266	
270	518	90667	86126	82882	80349	78264	76492	74944	73571	72336	
260	500	89768	85221	81970	79431	77340	75562	74007	72627	71386	
250	482	88850	84296	81038	78492	76393	74607	73046	71660	70411	
240	464	87914	83352	80087	77532	75426	73633	72064	70670	69413	
230	446	86957	82386	79112	76549	74434	72632	71054	69651	68386	
220	428	85980	81399	78116	75543	73418	71607	70019	68607	67332	
210	410	84979	80388	77094	74510	72375	70553	68955	67531	66246	
200	392	83957	79354	76048	73452	71305	69471	67861	66426	65128	
190	374	82912	78295	74975	72366	70206	68358	66734	65286	63975	
180	356	81839	77208	73873	71249	69073	67210	65572	64108	62782	
170	338	80740	76092	72740	70099	67906	66026	64371	62890	61547	
160	320	79612	74944	71573	68913	66702	64803	63128	61628	60266	
150	302	78454	73765	70372	67690	65467	63536	61840	60319	58935	
140	284	77264	72550	69133	66427	64170	62225	60504	58958	57550	
130	266	76038	71297	67852	65118	62832	60859	59111	57537	56101	
120	248	74776	70002	66525	63759	61442	59437	57656	56050	54583	
110	230	73473	68663	65149	62347	59993	57952	56134	54492	52988	
100	212	72127	67275	63720	60876	58479	56396	54538	52852	51304	
Saturation Temperature	C.	108.87	121.28	130.67	138.30	144.79	150.46	155.52	160.09	164.28	
	F.	227.97	250.31	267.21	280.94	292.62	302.83	311.93	320.16	327.71	

The characteristic (or figure before the decimal point) and the decimal point are omitted. The characteristic is always unity, except for the first four values under 20 lbs., and the first only under 80 lbs., for which the characteristic is 2.

The entropy is the same in all systems of units.

**TABLE VI.—ENTROPY  $\phi$  OF SUPERHEATED OR SUPERSATURATED STEAM  
IN THERMAL UNITS PER DEGREE, CENTIGRADE OR FAHRENHEIT.**

Pressure in pounds per sq. in. (Kg. per sq. cm. in italics)										
120 <i>8.4368</i>	140 <i>9.4830</i>	160 <i>11.242</i>	180 <i>13.655</i>	200 <i>16.061</i>	250 <i>20.577</i>	300 <i>26.092</i>	350 <i>32.607</i>	400 <i>40.123</i>	450 <i>48.638</i>	500 <i>58.154</i>
87744	86014	84511	83180	81987	79448	77357	75578	74024	72647	71403
84488	82747	81233	79891	78687	76120	74002	72105	70614	69267	67938
80972	79215	77685	76327	75107	72500	70342	68495	66874	65427	64118
80233	78472	76938	75576	74352	71735	69567	67710	66079	64622	63303
79482	77716	76177	74811	73583	70955	68776	66908	65266	63798	62468
78716	76946	75402	74031	72798	70158	67957	66087	64433	62953	61611
77939	76164	74615	73239	72001	69349	67145	65253	63586	62064	60739
77144	75363	73810	72428	71184	68518	66300	64394	62713	61207	59838
76334	74547	72987	71599	70349	67667	65434	63512	61816	60294	58910
75510	73717	72150	70755	69499	66800	64561	62612	60900	59361	57961
74670	72868	71295	69893	68629	65913	63645	61689	59958	58402	57083
73809	72000	70419	69009	67737	65009	62713	60737	58986	57409	55971
72930	71113	69523	68104	66823	64065	61755	59757	57984	56386	54925
72035	70208	68608	67180	65890	63108	60775	58733	56957	55335	53851
71117	69280	67669	66231	64930	62121	59762	57714	55891	54242	52732
70176	68327	66705	65255	63943	61106	58718	56641	54790	53113	51574
69213	67351	65717	64254	62929	60060	57640	55531	53648	51939	50368
68224	66348	64699	63222	61883	58978	56523	54378	52460	50715	49109
67210	65319	63654	62161	60807	57863	55369	53186	51228	49444	47799
66166	64257	62575	61065	59693	56706	54168	51941	49949	48113	46424
65093	63165	61464	59934	58543	55508	52922	50647	48508	46523	44986
63985	62036	60313	58763	57350	54261	51622	49294	47191	45202	43472
62844	60870	59123	57549	56112	52964	50264	47876	45713	43725	41874
61664	59663	57890	56288	54825	51609	48843	46387	44158	42103	40185
60440	58410	56606	54975	53481	50200	47348	44817	42512	40379	38388
59171	57107	55270	53604	52076	48790	45774	43157	40767	38550	36473
57852	55750	53874	52170	50604	47133	44110	41399	38914	36601	34428
56478	54332	52413	50666	49057	45478	42348	39527	36934	34514	32232
55044	52849	50881	49085	47428	43726	40474	37532	34816	32274	29872
53539	51289	49265	47413	45700	41859	38467	35386	32531	29859	27397
51957	49643	47555	45639	43863	39861	36310	33071	30057	27214	24513
50290	47903	45742	43754	41903	37720	33988	30563	27367	24345	21400
48625	46053	43809	41736	39803	35410	31467	27835	24429	21194	18102
171.75	178.31	184.16	189.48	194.36	205.10	214.32	222.45	229.75	236.42	242.57
344.15	352.96	363.49	373.07	381.85	401.19	417.78	432.41	445.55	457.56	468.63

Values below the black zigzag line represent supersaturated steam.  
 $\phi = 1.09876 \log (T/T_1) - 0.25356 \log (P/P_1) - \text{ancP}/T + 1.76300$ ,  
 where  $T_1 = 878.10^\circ$ ,  $P_1 = 14.6890$ , and the logs are to the base 10.



TABLE VII.—THERMODYNAMIC POTENTIAL,  $G = T\Phi - H$ , OF SUPERHEATED OR SUPERSATURATED STEAM, IN MEAN CALORIES CENTIGRADE.

Temperature.		Pressure in pounds per sq. in. (Kg. per sq. cm. in Italics.)								
		20	30	40	50	60	70	80	90	100
C.	F.	1.4091	2.1092	3.8123	5.5154	7.2184	8.9215	10.6246	12.3276	14.0307
500	932	772.65	738.16	713.69	694.71	679.20	666.11	654.75	644.75	635.81
450	842	669.63	637.33	614.51	596.77	582.27	570.03	559.42	550.07	541.72
400	752	568.26	538.24	516.97	500.47	486.99	475.62	465.75	457.07	449.31
390	734	548.18	518.63	497.67	481.42	468.14	456.95	447.24	438.71	431.04
380	716	528.19	499.08	478.44	462.44	449.37	438.34	428.78	420.36	412.85
370	698	508.28	479.62	458.30	443.55	430.68	419.83	410.42	402.13	394.73
360	680	488.44	460.22	440.22	424.72	412.07	401.38	392.12	383.97	376.69
350	662	468.65	440.91	421.23	405.97	393.52	383.01	373.90	365.88	358.72
340	644	448.96	421.66	402.30	387.30	375.05	364.71	355.76	347.88	340.83
330	626	429.38	402.49	383.46	368.71	356.67	346.51	337.70	329.95	323.03
320	608	409.82	383.42	364.70	350.20	338.37	328.38	319.73	312.10	305.31
310	590	390.37	364.41	346.03	331.78	320.15	310.33	301.83	294.35	287.67
300	572	370.99	345.50	327.43	313.44	302.00	292.37	284.03	276.67	270.12
290	554	351.72	326.67	308.92	295.18	283.96	274.50	266.31	259.10	252.66
280	536	332.52	307.93	290.50	277.01	266.00	256.72	248.67	241.60	235.29
270	518	313.41	289.26	272.16	258.92	248.13	239.01	231.13	224.19	218.01
260	500	294.38	270.70	253.92	240.94	230.34	221.42	213.68	206.89	200.82
250	482	275.45	252.22	235.78	222.94	212.65	203.91	196.33	189.66	183.73
240	464	256.62	233.84	217.72	205.25	195.07	186.50	179.08	172.56	166.74
230	446	237.88	215.56	199.76	187.54	177.58	169.18	161.93	155.54	149.86
220	428	219.23	197.36	181.90	169.93	160.18	151.97	144.87	138.62	133.07
210	410	200.66	179.26	164.12	152.42	142.88	134.86	127.91	121.81	116.38
200	392	182.22	161.28	146.47	135.02	125.70	117.85	111.07	105.11	99.81
190	374	163.88	143.39	128.92	117.73	108.63	100.96	94.34	88.53	83.35
180	356	145.65	125.63	111.48	100.55	91.66	84.19	77.73	72.06	67.02
170	338	127.51	107.95	94.14	83.48	74.79	67.53	61.23	55.71	50.80
160	320	109.49	90.41	76.93	66.54	58.08	50.98	44.85	39.48	34.71
150	302	91.59	72.97	59.83	49.70	41.47	34.56	28.60	23.38	18.75
140	284	73.80	55.65	42.86	32.99	24.98	18.27	+12.48	+7.41	+2.92
130	266	56.14	38.46	26.00	+16.41	+8.63	+2.11	-3.50	-8.41	-12.77
120	248	37.59	21.38	+9.28	-0.03	-7.58	-13.91	19.34	24.99	28.30
110	230	21.18	+4.46	-7.30	16.34	23.65	29.77	35.03	39.62	43.68
100	212	+3.89	-12.35	23.76	32.51	39.58	45.49	50.58	55.00	58.90
Saturation	C.	108.87	121.28	130.67	138.30	144.79	150.46	155.52	160.09	164.28
Temperature	F.	227.97	250.31	267.21	280.94	292.62	302.83	311.93	320.16	327.71

The sign of  $G$  changes from positive to negative a little below the saturation line, as indicated by the signs + and -.

$$G = S_0 T \log_e (T/T_1) - RT \log_e (P/P_1) + a(c-b)P_1 + (\Phi_1 - S_0)T - B$$

where  $T_1 = 373.10^\circ$ ,  $P_1 = 14.6990$  lbs.,  $\Phi_1 = 1.76800$ ,  $B = 464.00$ ,  $S_0 = 0.47719$ .

**TABLE VII.—THERMODYNAMIC POTENTIAL,  $G = T\Phi - H$ , OF SUPERHEATED OR SUPERSATURATED STEAM, IN MEAN CALORIES CENTIGRADE.**

Pressure in pounds per sq. in. (Kg. per sq. cm. in italics.)										
120 <i>8.4563</i>	140 <i>9.4880</i>	160 <i>11.219</i>	180 <i>13.255</i>	200 <i>15.061</i>	250 <i>17.577</i>	300 <i>21.092</i>	350 <i>24.007</i>	400 <i>26.123</i>	450 <i>31.638</i>	500 <i>35.161</i>
620.32	607.24	595.93	585.93	577.02	558.12	542.70	529.70	518.44	508.51	499.6
527.27	515.06	504.48	495.10	486.84	469.22	454.86	442.76	432.28	423.05	414.8
435.88	424.55	414.74	406.00	398.37	382.05	368.75	357.55	347.88	339.36	331.7
417.82	406.66	397.00	388.50	380.90	364.84	351.75	340.74	331.24	322.85	315.4
399.83	388.85	379.35	370.97	363.50	347.70	334.84	324.01	314.66	306.44	299.1
381.92	371.12	361.76	353.53	346.18	330.65	318.00	307.36	298.18	290.10	282.9
364.08	353.46	344.27	336.17	328.95	313.67	301.24	290.79	281.78	273.84	266.7
346.33	335.88	326.84	318.87	311.78	296.77	284.57	274.31	265.46	257.68	250.7
328.66	318.38	309.50	301.67	294.70	279.96	267.98	257.91	249.23	241.60	234.8
311.06	300.96	292.25	284.56	277.70	263.23	251.48	241.60	233.69	225.60	218.0
293.55	283.63	275.07	267.53	260.80	246.60	235.07	225.39	217.05	208.55	203.2
276.13	266.39	257.98	250.57	243.98	230.07	218.75	209.27	201.10	193.94	187.5
258.79	249.23	240.98	233.72	227.24	213.60	202.53	193.24	185.26	178.24	172.0
241.54	232.18	224.08	216.96	210.62	197.25	186.40	177.32	169.51	162.67	156.6
224.38	215.20	207.26	200.29	194.07	180.99	170.38	161.50	153.87	147.18	141.2
207.31	198.32	190.54	183.71	177.63	164.82	154.45	145.78	138.34	131.81	126.0
190.34	181.54	173.93	167.24	161.29	148.77	138.63	130.17	122.91	116.56	110.9
173.47	164.84	157.40	150.86	145.04	132.80	122.92	114.67	107.60	101.42	95.9
156.71	148.27	140.98	134.60	128.91	116.96	107.33	99.30	92.42	86.42	81.1
140.04	131.79	124.68	118.43	112.89	101.24	91.86	84.04	77.36	71.55	66.4
123.47	115.41	108.47	102.38	96.97	85.63	76.50	68.91	62.43	56.90	51.8
107.01	99.14	92.38	86.44	81.16	70.13	61.26	53.74	47.64	42.19	37.4
90.67	83.00	76.40	70.63	65.50	54.77	46.17	39.04	32.99	27.75	23.1
74.44	66.97	60.55	54.93	49.95	39.54	31.21	24.32	18.50	+13.45	+9.0
58.35	51.07	44.83	39.38	34.55	24.56	16.41	+5.77	+4.17	-0.67	-4.1
42.36	35.29	29.24	23.94	19.26	+9.51	+1.74	-4.64	-10.01	-14.62	-18.0
26.51	+19.65	+13.77	+8.66	+4.12	-5.28	-12.75	-18.86	-23.99	28.48	32.1
+10.78	+4.14	-1.54	-6.50	-10.87	-19.93	-27.07	32.91	37.78	41.94	45.4
-4.80	-11.22	-16.71	-21.48	-25.69	34.39	41.22	46.77	51.38	55.29	58.9
20.22	-20.43	31.72	36.31	40.35	48.67	55.19	60.42	64.74	68.39	71.4
35.49	41.48	46.57	50.96	54.84	62.76	68.91	73.84	77.87	81.24	84.0
50.61	56.36	61.22	65.43	69.11	76.63	82.42	87.02	90.75	93.82	96.1
65.56	71.06	75.71	79.72	83.21	90.30	95.70	99.95	103.36	106.11	108.4
171.75	178.31	184.16	189.48	194.36	205.10	214.32	222.45	229.75	236.42	242.1
341.15	352.96	363.49	373.07	381.85	401.19	417.78	432.41	445.55	457.56	468.1

To reduce to B.Th.U. Fahr., subtract a tenth and multiply by 2.  
 No reduction required for Metric Units (K.M.C.).  
 Values below the black zigzag line represent supersaturated steam.

TABLE VIII.—ADIABATIC HEAT-DROP TO 1 LB. ABS. IN CALS. C. FROM INITIAL STATES:—

Temperature		Initial Pressures in Lbs. per Sq. In. Abs.									
C.	F.	15	20	30	40	50	60	70	80	90	100
500	932	177.94	187.77	201.57	211.31	218.90	225.00	230.25	234.74	238.69	242.1
450	842	163.97	173.78	187.57	197.32	204.86	211.01	216.18	220.66	224.58	228.1
400	752	150.89	160.50	174.31	184.01	191.52	197.62	202.78	207.24	211.07	214.5
390	734	148.16	157.96	171.71	181.46	188.96	195.07	200.18	204.60	208.49	211.9
380	716	145.64	155.43	169.18	178.91	186.40	192.51	197.60	202.04	205.93	209.3
370	698	143.13	152.93	166.68	176.40	183.87	189.99	195.07	199.51	203.39	206.8
360	680	140.69	150.48	164.23	173.93	181.40	187.47	192.58	197.01	200.85	204.2
350	662	138.28	148.07	161.80	171.49	178.95	185.03	190.13	194.54	198.39	201.8
340	644	135.90	145.68	159.39	169.09	176.55	182.62	187.69	192.10	195.94	199.3
330	626	133.57	143.34	157.04	166.72	174.18	180.22	185.30	189.69	193.51	196.9
320	608	131.28	141.05	154.73	164.39	171.84	177.88	182.94	187.31	191.12	194.5
310	590	129.01	138.78	152.48	162.10	169.54	175.58	180.62	185.00	188.79	192.1
300	572	126.80	136.55	150.24	159.87	167.28	173.33	178.37	182.71	186.50	189.8
290	554	126.64	134.39	148.06	157.67	165.07	171.09	176.13	180.45	184.24	187.5
280	536	122.50	132.25	145.90	155.52	162.90	168.90	173.94	178.24	182.01	185.3
270	518	120.43	130.17	143.81	153.41	160.79	166.74	171.77	176.07	179.84	183.1
260	500	118.41	128.14	141.75	151.35	158.70	164.67	169.66	173.96	177.70	181.0
250	482	116.42	126.14	139.76	149.32	156.67	162.62	167.60	171.88	175.62	178.9
240	464	114.50	124.21	137.80	147.36	154.68	160.63	165.58	169.84	173.56	176.8
230	446	112.64	122.34	135.91	145.43	152.76	158.67	163.63	167.85	171.57	174.8
220	428	110.81	120.51	134.08	143.59	150.89	156.79	161.72	165.94	169.64	172.8
210	410	109.07	118.76	132.31	141.79	149.06	154.96	159.87	164.07	167.73	170.9
200	392	107.38	117.06	130.57	140.06	147.32	153.17	158.07	162.26	165.90	169.0
190	374	105.73	115.40	128.91	138.35	145.61	151.44	156.31	160.47	164.08	167.25
180	356	104.17	113.83	127.31	136.74	143.97	149.78	154.62	158.77	162.37	165.51
170	338	102.69	112.34	125.80	135.21	142.40	148.22	153.01	157.13	160.71	163.86
160	320	101.28	110.92	124.33	133.72	140.89	146.67	151.47	155.57	159.12	162.24
150	302	99.94	109.56	122.97	132.33	139.49	145.23	150.01	154.07	157.55	160.60
140	284	98.60	108.30	121.68	131.01	138.15	143.86	148.55	152.54	155.96	158.94
130	266	97.54	107.13	120.48	129.80	136.85	142.47	147.09	150.99	154.32	157.24
120	248	96.47	106.05	119.35	128.59	135.54	141.07	145.59	149.41	152.68	155.51
110	230	95.45	105.02	118.27	127.38	134.22	139.64	144.08	147.81	150.98	153.73
100	212	94.56	104.11	117.18	126.15	132.87	138.20	142.52	146.16	149.25	151.91
Dry (DH, C.)		94.64	104.95	119.50	129.87	137.92	144.53	150.07	154.90	159.16	162.92
Sat. (F.)		100.58	108.87	121.28	130.67	138.30	144.79	150.46	155.62	160.09	164.28
		213.04	227.97	250.31	267.21	280.94	292.62	302.83	311.93	320.16	327.71

$DH_s = (t' - t'')h' - (G' - G'')$ .  $t' = 38.74^\circ \text{C}$ .  $G'' = 2.61$  cals. C. The final state is taken as wet saturated at 1 lb./in.<sup>2</sup> abs.

TABLE VIII.—ADIABATIC HEAT-DROP TO 1 LB. ABS. IN CALS. C. FROM INITIAL STATES:—

Initial Pressures in Lbs. per Sq. In. Abs.										
120	140	160	180	200	250	300	350	400	450	5
248.27	253.37	257.77	261.63	265.05	272.23	278.01	282.81	286.86	290.47	28
234.10	239.14	243.48	247.29	250.68	257.72	263.36	268.42	272.00	275.47	27
220.52	225.51	229.78	233.55	236.86	243.74	249.25	253.77	257.59	260.90	26
217.89	222.87	227.15	230.88	234.16	241.02	246.50	250.98	254.76	258.03	26
215.30	220.25	224.51	228.22	231.49	238.32	243.77	248.21	251.95	255.17	25
212.74	217.65	221.90	225.59	228.85	235.65	241.05	245.46	249.16	252.38	25
210.20	215.10	219.32	223.01	226.24	233.01	238.34	242.72	246.40	249.62	25
207.67	212.58	216.80	220.45	223.66	230.40	235.69	240.00	243.66	246.71	24
205.18	210.10	214.28	217.93	221.13	227.80	233.04	237.31	240.92	243.99	24
202.76	207.65	211.78	215.42	218.62	225.32	230.42	234.65	238.19	241.18	24
200.36	205.22	209.33	212.94	216.12	222.68	227.82	232.01	235.49	238.44	24
197.97	202.81	206.93	210.51	213.67	220.16	225.25	229.30	232.80	235.70	23
195.64	200.44	204.54	208.09	211.23	217.63	222.69	226.78	230.13	232.97	23
193.33	198.12	202.21	205.71	208.82	215.19	220.17	224.18	227.48	230.25	23
191.09	195.84	199.90	203.39	206.47	212.77	217.69	221.62	224.85	227.67	22
188.88	193.59	197.60	201.08	204.13	210.39	215.24	219.10	222.26	224.90	22
186.68	191.37	195.38	198.81	201.83	208.02	212.80	216.59	219.69	222.25	22
184.54	189.18	193.18	196.59	199.59	205.70	210.39	214.10	217.12	219.61	22
182.45	187.08	191.01	194.39	197.37	203.38	208.00	211.63	214.57	216.97	21
180.41	185.00	188.88	192.25	195.17	201.10	205.64	209.19	212.04	214.35	21
178.40	182.97	186.82	190.14	193.01	198.88	203.31	206.77	209.50	211.75	21
176.46	180.98	184.80	188.09	190.92	196.68	201.04	204.33	206.90	208.89	21
174.55	179.05	182.83	186.07	188.87	194.51	198.68	201.81	204.21	206.64	20
172.70	177.14	180.88	184.08	186.84	192.31	196.28	199.23	201.44	203.09	20
170.90	175.31	179.00	182.14	184.80	190.05	193.93	196.57	198.59	200.03	20
169.19	173.52	177.09	180.13	182.70	187.73	191.27	193.81	195.62	196.85	19
167.47	171.68	175.16	178.09	180.56	185.31	188.64	190.96	192.54	193.55	19
165.70	169.81	173.19	175.99	178.35	182.87	185.94	187.99	189.32	190.07	19
163.91	167.89	171.13	173.83	176.09	180.33	183.12	184.90	185.96	186.44	18
162.07	165.93	169.03	171.61	173.74	177.67	180.17	181.65	182.41	182.61	18
160.30	163.89	166.87	169.31	171.30	174.91	177.07	178.23	178.67	178.54	17
158.55	161.81	164.63	166.93	168.77	172.03	173.83	174.64	174.71	174.23	17
156.77	159.65	162.31	164.45	166.13	168.99	170.40	170.81	170.49	169.61	16
155.00	157.50	160.00	162.30	164.30	166.80	168.50	169.50	169.50	168.50	15
153.25	155.37	157.37	159.27	160.97	162.87	164.37	165.37	165.37	164.37	14
151.50	153.25	154.87	156.37	157.77	159.37	160.67	161.37	161.37	160.37	13
149.75	151.12	152.47	153.77	154.97	156.37	157.37	157.37	156.37	155.37	12
148.00	149.00	150.00	150.97	151.87	152.87	153.57	153.57	152.57	151.57	11
146.25	147.00	147.62	148.12	148.52	148.92	149.12	149.12	148.12	147.12	10
144.50	145.00	145.37	145.62	145.87	146.12	146.27	146.27	145.27	144.27	9
142.75	143.00	143.12	143.27	143.37	143.47	143.52	143.52	142.52	141.52	8
141.00	141.12	141.17	141.22	141.27	141.32	141.32	141.32	140.32	139.32	7
139.25	139.25	139.25	139.25	139.25	139.25	139.25	139.25	138.25	137.25	6
137.50	137.37	137.25	137.12	136.97	136.82	136.67	136.52	136.37	136.22	5
135.75	135.50	135.25	135.00	134.75	134.50	134.25	134.00	133.75	133.50	4
134.00	133.62	133.25	132.87	132.50	132.12	131.75	131.37	131.00	130.62	3
132.25	131.75	131.25	130.75	130.25	129.75	129.25	128.75	128.25	127.75	2
130.50	130.00	129.37	128.75	128.12	127.50	126.87	126.25	125.62	125.00	1
128.75	128.12	127.37	126.62	125.87	125.12	124.37	123.62	122.87	122.12	0
127.00	126.25	125.50	124.75	124.00	123.25	122.50	121.75	121.00	120.25	-1
125.25	124.37	123.50	122.62	121.75	120.87	120.00	119.12	118.25	117.37	-2
123.50	122.50	121.50	120.50	119.50	118.50	117.50	116.50	115.50	114.50	-3
121.75	120.62	119.50	118.37	117.25	116.12	115.00	113.87	112.75	111.62	-4
120.00	118.75	117.50	116.25	115.00	113.75	112.50	111.25	110.00	108.75	-5
118.25	116.87	115.50	114.12	112.75	111.37	110.00	108.62	107.25	105.87	-6
116.50	115.00	113.50	112.00	110.50	109.00	107.50	106.00	104.50	103.00	-7
114.75	113.12	111.50	110.00	108.50	107.00	105.50	104.00	102.50	101.00	-8
113.00	111.25	109.50	107.75	106.00	104.25	102.50	100.75	99.00	97.25	-9
111.25	109.37	107.50	105.62	103.75	101.87	100.00	98.12	96.25	94.37	-10
109.50	107.50	105.50	103.50	101.50	99.50	97.50	95.50	93.50	91.50	-11
107.75	105.62	103.50	101.37	99.25	97.12	95.00	92.87	90.75	88.62	-12
106.00	103.75	101.50	99.25	97.00	94.75	92.50	90.25	88.00	85.75	-13
104.25	101.87	99.50	97.12	94.75	92.37	90.00	87.62	85.25	82.87	-14
102.50	100.00	97.50	95.00	92.50	90.00	87.50	85.00	82.50	80.00	-15
100.75	98.12	95.50	92.87	90.25	87.62	85.00	82.37	79.75	77.12	-16
99.00	96.25	93.50	90.75	88.00	85.25	82.50	79.75	77.00	74.25	-17
97.25	94.37	91.50	88.62	85.75	82.87	80.00	77.12	74.25	71.37	-18
95.50	92.50	89.50	86.50	83.50	80.50	77.50	74.50	71.50	68.50	-19
93.75	90.62	87.50	84.37	81.25	78.12	75.00	71.87	68.75	65.62	-20
92.00	88.75	85.50	82.25	79.00	75.75	72.50	69.25	66.00	62.75	-21
90.25	86.87	83.50	80.12	76.75	73.37	70.00	66.62	63.25	59.87	-22
88.50	85.00	81.50	78.00	74.50	71.00	67.50	64.00	60.50	57.00	-23
86.75	83.12	79.50	75.87	72.25	68.62	65.00	61.37	57.75	54.12	-24
85.00	81.37	77.75	74.12	70.50	66.87	63.25	59.62	56.00	52.37	-25
83.25	79.62	76.00	72.37	68.75	65.12	61.50	57.87	54.25	50.62	-26
81.50	77.75	74.12	70.50	66.87	63.25	59.62	56.00	52.37	48.75	-27
79.75	75.87	72.25	68.62	65.00	61.37	57.75	54.12	50.50	46.87	-28
78.00	74.00	70.37	66.75	63.12	59.50	55.87	52.25	48.62	45.00	-29
76.25	72.12	68.50	64.87	61.25	57.62	54.00	50.37	46.75	43.12	-30
74.50	70.25	66.62	63.00	59.37	55.75	52.12	48.50	44.87	41.25	-31
72.75	68.37	64.75	61.12	57.50	53.87	50.25	46.62	43.00	39.37	-32
71.00	66.50	62.87	59.25	55.62	52.00	48.37	44.75	41.12	37.50	-33
69.25	64.62	61.00	57.37	53.75	50.12	46.50	42.87	39.25	35.62	-34
67.50	62.75	59.12	55.50	51.87	48.25	44.62	41.00	37.37	33.75	-35
65.75	60.87	57.25	53.62	50.00	46.37	42.75	39.12	35.50	31.87	-36
64.00	59.00	55.37	51.75	48.12	44.50	40.87	37.25	33.62	30.00	-37
62.25	57.12	53.50	49.87	46.25	42.62	39.00	35.37	31.75	28.12	-38
60.50	55.25	51.62	48.00	44.37	40.75	37.12	33.50	29.87	26.25	-39
58.75	53.37	49.75	46.12	42.50	38.87	35.25	31.62	28.00	24.37	-40
57.00	51.50	47.87	44.25	40.62	37.00	33.37	29.75	26.12	22.50	-41
55.25	49.62	46.00	42.37	38.75	35.12	31.50	27.87	24.25	20.62	-42
53.50	47.75	44.12	40.50	36.87	33.25	29.62	26.00	22.37	18.75	-43
51.75	45.87	42.25	38.62	35.00	31.37	27.75	24.12	20.50	16.87	-44
50.00	44.00	40.37	36.75	33.12	29.50	25.87	22.25	18.62	15.00	-45
48.25	42.12	38.50	34.87	31.25	27.62	24.00	20.37	16.75	13.12	-46
46.50	40.25	36.62	33.00	29.37	25.75	22.12	18.50	14.87	11.25	-47
44.75	38.37	34.75	31.12	27.50	23.87	20.25	16.62	13.00	9.37	-48
43.00	36.50	32.87	29.25	25.62	22.00	18.37	14.75	11.12	7.50	-49
41.25	34.62	31.00	27.37	23.75	20.12	16.50	12.87	9.25	5.62	-50
39.50	32.75	29.12	25.50	21.87	18.25	14.62	11.00	7.37	3.75	-51
37.75	30.87	27.25	23.62	19.00	16.37	12.75	9.12	5.50	1.87	-52
36.00	29.00	25.37	21.75	17.12	14.50	10.87	7.25	3.62	0.00	-53
34.25	27.12	23.50	19.87	15.25	12.62	9.00	5.37	1.75</		

• TABLE IX.—VALUES OF 100 SC (CALORIES CENT. PER 100 LBS. PRESSURE).

Temperature		Values of 100 SC for each degree Centigrade.									
C.	F.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
100	212	18.61	18.45	18.29	18.13	17.97	17.81	17.66	17.50	17.34	17.18
110	230	17.03	16.88	16.73	16.58	16.44	16.30	16.17	16.03	15.90	15.76
120	248	15.62	15.49	15.36	15.23	15.10	14.97	14.85	14.72	14.59	14.46
130	266	14.34	14.22	14.10	13.99	13.87	13.76	13.65	13.54	13.43	13.32
140	284	13.21	13.11	13.00	12.90	12.80	12.70	12.59	12.49	12.39	12.29
150	302	12.19	12.09	12.00	11.91	11.82	11.72	11.63	11.53	11.44	11.35
160	320	11.26	11.17	11.08	11.00	10.91	10.82	10.74	10.66	10.58	10.50
170	338	10.42	10.34	10.26	10.18	10.11	10.03	9.96	9.88	9.81	9.73
180	356	9.66	9.59	9.52	9.45	9.38	9.31	9.24	9.18	9.11	9.04
190	374	8.97	8.91	8.84	8.78	8.71	8.65	8.59	8.52	8.46	8.40
200	392	8.34	8.28	8.22	8.16	8.10	8.05	7.99	7.93	7.88	7.82
210	410	7.77	7.71	7.65	7.60	7.54	7.49	7.44	7.39	7.34	7.29
220	428	7.24	7.19	7.14	7.09	7.04	7.00	6.95	6.90	6.85	6.80
230	446	6.76	6.71	6.67	6.62	6.58	6.53	6.49	6.45	6.40	6.36
240	464	6.32	6.28	6.24	6.20	6.16	6.12	6.08	6.04	6.00	5.96
250	482	5.92	5.88	5.84	5.80	5.76	5.72	5.69	5.65	5.61	5.57
260	500	5.54	5.50	5.47	5.43	5.40	5.37	5.33	5.30	5.26	5.23
270	518	5.20	5.16	5.13	5.10	5.07	5.04	5.01	4.98	4.95	4.92
280	536	4.89	4.86	4.83	4.80	4.77	4.74	4.72	4.69	4.66	4.63
290	554	4.60	4.57	4.54	4.51	4.49	4.46	4.43	4.40	4.37	4.35
300	572	4.32	4.30	4.27	4.25	4.22	4.20	4.17	4.15	4.13	4.10
310	590	4.07	4.05	4.03	4.00	3.98	3.95	3.93	3.91	3.88	3.86
320	608	3.84	3.81	3.79	3.77	3.74	3.72	3.70	3.68	3.66	3.64
330	626	3.62	3.60	3.58	3.56	3.54	3.52	3.50	3.48	3.46	3.44
340	644	3.42	3.40	3.38	3.36	3.34	3.32	3.30	3.29	3.27	3.25
350	662	3.23	3.21	3.19	3.18	3.16	3.15	3.13	3.11	3.10	3.08
360	680	3.06	3.04	3.03	3.01	2.99	2.98	2.96	2.95	2.93	2.91
370	698	2.89	2.88	2.86	2.85	2.83	2.82	2.80	2.79	2.77	2.76
380	716	2.74	2.73	2.71	2.70	2.68	2.67	2.65	2.64	2.62	2.61
390	734	2.60	2.58	2.57	2.56	2.54	2.53	2.51	2.50	2.48	2.47
400	752	2.46	2.44	2.43	2.42	2.40	2.39	2.38	2.36	2.35	2.34
		0	1.8	3.6	5.4	7.2	9.0	10.8	12.6	14.4	16.2

EQUIVALENT DEGREES AND DECIMALS FAHRENHEIT.

## INDEX OF PARTIAL DIFFERENTIAL COEFFICIENTS OF $E, G, H, P, Q, \Phi, T$ , AND $V$

To find a general expression for any coefficient in terms of the specific heat at  $S$  at constant pressure, and the cooling effects, namely:

$C = C_H = (dT/dP)_H$ , in a throttling process at constant  $H$ .

$C_Q = C_\Phi = (dT/dP)_\Phi$ , in adiabatic expansion at constant  $\Phi$ .

$C_V = (dT/dP)_V = 1/(dP/dT)_V$ , in cooling at constant volume.

$C_S = (dT/dP)_S = 1/(dp/dt)$ , in expansion of a saturated vapour.

$C_E = (dT/dP)_E = C_\Phi (1 - C_V P/T)/(1 - C_\Phi P/T)$ , in expansion at constant  $E$ .

$C_G = (dT/dP)_G = aV/\Phi$ , in expansion at constant potential  $G$ .

The last two cannot be measured experimentally, but are easily calculated.

(1) The six coefficients of the type  $(dX/dT)_P$  are as follows:

$$\left. \begin{aligned} (dH/dT)_P &= (dQ/dT)_P = T (d\Phi/dT)_P + S \\ (dV/dT)_P &= V/T + SC/aT = SC_\Phi/aT \\ (dE/dT)_P &= S(1 - C_\Phi P/T); (dG/dT)_P = -\Phi \end{aligned} \right\} \dots\dots(1)$$

(2) In terms of the above six, any coefficient with respect to  $T$  or  $P$  can be written down by the general relation:

$$C_Z (dX/dT)_Z = (dX/dP)_Z = (dX/dT)_P (C_Z - C_X) \dots\dots(2)$$

(3) Any other coefficient is given by the ratio of two of the above:

$$(dX/dY)_Z = \frac{(dX/dP)_Z}{(dY/dP)_Z} = \frac{(dX/dT)_P (C_Z - C_X)}{(dY/dT)_P (C_Z - C_Y)} \dots\dots(3)$$

When  $Z = P$ , this reduces to  $(dX/dT)_P/(dY/dT)_P$ , since  $C_P$  is infinite.

When  $Z = T$ , it becomes  $(C_X/C_Y) (dX/dT)_P/(dY/dT)_P$ , since  $C_T$  is zero.

(4) These expressions may be transformed by the general relations:

$$\left. \begin{aligned} C_\Phi &= a (dV/d\Phi)_P = aT (dV/dT)_P/S = C + aV/S \\ C_V &= a (dV/d\Phi)_T = -aT (dV/dT)_\Phi/S_V = S (C_V - C_\Phi)/S_V \end{aligned} \right\} \dots\dots(4)$$

## 522 INDEX OF PARTIAL DIFFERENTIAL COEFFICIENTS

(5) The special relations for Dry Steam are as follows:

$$\left. \begin{aligned} C &= SC/S = C_E - ab/S &= C_\phi - aV/S &= C_V - (H - B)/SP \\ C_E &= 13ac/3S = C + ab/S &= C_\phi - a(V - b)/S &= C_V acP/RT \\ C_\phi &= 3T/13P = C + aV/S &= acT/SPC_E &= 3S_0 C_V/13S \\ C_V &= S_0 T/SP = C + (H - B)/6P = C_E RT/acP &= C_\phi + (E - B)/SP \\ C_S &= 3VT/(H - st) = avT/(h - st) \text{ (wet or dry saturated).} \end{aligned} \right\} \dots\dots(5)$$

$$S = S_0 + 14.4acP/T, S_0 = 13R/3 = 0.4772, B = 464 \text{ cal.}, C = 835.2 \text{ B.Th.U.}$$

NOTE. When  $S_0$  is known by experiment  $S - S_0$ ,  $SC$ ,  $C_V$ , and  $C_\phi$  may be deduced from the characteristic equation; or conversely, the characteristic equation may be verified by experimental measurements of  $C_V$  and  $C$ , or  $C_\phi$ ; and any other coefficient which may be required can be obtained from (3) as shown in the following list. The omission of the value for dry steam in any case may be taken to imply that the general expression does not simplify materially on substituting the special values from (5). In such a case it is preferable to calculate the coefficient by inserting the appropriate numerical values of  $S$ ,  $C_V$ , etc. in the general expression. The suffix  $S$  refers to the state of saturation. The suffix  $Z$  stands for any suffix, including  $S$ .  $X$  and  $Y$  represent any two of the six quantities,  $E$ ,  $G$ ,  $H$ ,  $Q$ ,  $\Phi$ , and  $V$ .

# INDEX OF COEFFICIENTS

Coefficient	General Expression	Value for Dry Steam
$(dE/dG)_P$	$S(1 - C_\phi P/T)/\Phi$	$10S/13\Phi$
$(dE/dG)_\phi$	$S_V C_V P/T (\Phi - aV/C_\phi)$	$(E - B)/(T\Phi - 13aPV/3)$
$(dE/dG)_T$	$SC_\phi(1 - C_V P/T)/aV$	$10c/3V$
$(dE/dG)_V$	$S_V C_V/(C_V\Phi - aV)$	$(E - B)/(S_V T\Phi/S - aPV)$
$(dE/dH)_P$	$1 - C_\phi P/T$	$10/13$
$(dE/dH)_\phi$	$S_V C_V C_\phi P/aVT$	$10(V - b)/13V$
$(dE/dH)_T$	$(1 - C_V P/T) C_\phi/C$	$10/(13 - 3b/c)$
$(dE/dH)_V$	$(C_V - C_\phi)/(C_V - C)$	$10/(13 - 3b/(V - b))$
$(dE/dP)_H$	$SC_\phi(C_V - C)P/T - aV$	$10ab/13$
$(dE/dP)_\phi$	$S_V C_V C_\phi P/T$	$10a(V - b)/13$
$(dE/dP)_T$	$-SC_\phi(1 - C_V P/T)$	$-10ac/3$
$(dE/dP)_V$	$S_V C_V - S(C_V - C_\phi)$	$(E - B)/P - 10a(V - b)/3$
$(dE/dQ)_Z$	$(1/T)(dE/d\Phi)_Z$	See $(dE/d\Phi)$
$(dE/d\Phi)_H$	$T - C_\phi P(C_V - C)/(C_\phi - C)$	$10bT/13V$
$(dE/d\Phi)_P$	$T - C_\phi P$	$10T/13$
$(dE/d\Phi)_T$	$T - C_V P$	$130acP/9S$
$(dE/d\Phi)_V$	$T$	$T$
$(dE/dT)_G$	$S(1 - C_\phi P/T)(1 - C_E/C_G)$	$10S/13 - 10c\Phi/3V$
$(dE/dT)_H$	$S(1 - C_\phi P/T)(1 - C_E/C)$	$-(10S/13)/(13c/3b - 1)$
$(dE/dT)_P$	$S(1 - C_\phi P/T)$	$10S/13$
$(dE/dT)_\phi$	$SP(C_V - C_\phi)$	$(E - B)/T$
$(dE/dT)_V$	$S_V = S(C_V - C_\phi)/C_V$	$(10S/13)(1 - acP/RT)$
$(dE/dV)_H$	$(aT/C_\phi - aP)(C_E - C)/(C_V - C)$	$aP/(13V/10b - 1)$
$(dE/dV)_P$	$aT/C_\phi - aP$	$10aP/3$
$(dE/dV)_\phi$	$-aP$	$-aP$
$(dE/dV)_T$	$aT/C_V - aP$	$aP(10acP/3RT)$
$(dG/dE)_Z$	$1/(dE/dG)_Z$	See Reciprocals above
$(dG/dH)_\phi$	$\Phi(C_E - C_G)/(C_E - C)$	$13c\Phi/3bS - V/b$
$(dG/dH)_P$	$\Phi/S$	$\Phi/S$
$(dG/dH)_\phi$	$C_\phi\Phi/aV - 1$	$3T\Phi/13aPV - 1$
$(dG/dH)_T$	$aV/SC$	$V/(13c/3 - b)$
$(dG/dH)_V$	$(\Phi C_V - aV)/(SC_V - SC)$	$(S_V T\Phi/S - aPV)/(H - B)$



## INDEX OF COEFFICIENTS

Coefficient	General Expression	Value for Dry Steam
$(dG/dP)_E$	$\Phi (C_E - C_G)$	$18cc\Phi/3S - aV$
$(dG/dP)_H$	$C\Phi - aV$	$(18ac/3 - ab)\Phi/S - aV$
$(dG/dP)_\Phi$	$\Phi (C_\Phi - C_G)$	$3T\Phi/13P - aV$
$(dG/dP)_T$	$-aV$	$-aV$
$(dG/dP)_V$	$\Phi C_V - aV$	$S_0T\Phi/SP - aV$
$(dG/dP)_S$	$\Phi (C_S - C_G)$	$aV (T\Phi/(H - st) - 1)$
$(dG/d\Phi)_E$	$T\Phi (C_E - C_G)/(C_E - C_\Phi) S$	$T (V - 18c\Phi/3S)/(V - b)$
$(dG/d\Phi)_H$	$T (1 - C\Phi/aV)$	$T (1 - C\Phi/aV)$
$(dG/d\Phi)_P$	$T\Phi/S$	$T\Phi/S$
$(dG/d\Phi)_T$	$aVT/SC_\Phi$	$13aPV/3S$
$(dG/d\Phi)_V$	$(T\Phi C_V - aVT)/S_V C_V$	$T (S_0T\Phi/S - aPV)/(E - B)$
$(dG/dT)_E$	$\Phi (1 - C_G/C_E)$	$\Phi - 3VS/13c$
$(dG/dT)_H$	$\Phi (1 - C_G/C)$	$\Phi - aV/C$
$(dG/dT)_P$	$\Phi$	$\Phi$
$(dG/dT)_\Phi$	$\Phi - bV/C_\Phi$	$\Phi - 13aPV/3T$
$(dG/dT)_V$	$\Phi - aV/C_V$	$\Phi - SaPV/S_0T$
$(dG/dT)_S$	$\Phi - aV dp/dt$	$\Phi - (I - st)/T$
$(dG/dV)_E$	$aT\Phi (C_E - C_G)/SC_\Phi (C_E - C_V)$	$P (aV - C_E\Phi)/(V - b)$
$(dG/dV)_H$	$aT\Phi (C - C_G)/SC_\Phi (C - C_V)$	$P (aV - C\Phi)/(V - 10b/13)$
$(dG/dV)_P$	$aT\Phi/SC_\Phi = \Phi (dT/dV)_P$	$13aP\Phi/3S$
$(dG/dV)_\Phi$	$aT\Phi (C_\Phi - C_G)/SC_\Phi (C_\Phi - C_V)$	
$(dG/dV)_T$	$aT\Phi C_G/SC_\Phi C_V$	$aP (aPV/RT)$
$(dH/dE)_Z$	$1/(dE/dH)_Z$	See Reciprocals
$(dH/dG)_Z$	$1/(dG/dH)_Z$	" "
$(dH/dP)_E$	$S (C_E - C)$	$ab$
$(dH/dP)_G$	$S (C_G - C)$	$aVS/\Phi - SC$
$(dH/dP)_\Phi$	$aV$	$aV$
$(dH/dP)_T$	$-SC$	$-13ac/3 + ab$
$(dH/dP)_V$	$S (C_V - C)$	$(H - B)/P = 13aV - 10ab$
$(dH/dP)_S$	$S (C_S - C)$	$SaVT/(H - st) - SC_\Phi$
$(dH/d\Phi)_E$	$T (C_E - C)/(C_E - C_\Phi)$	$-Tb/(V - b)$
$(dH/d\Phi)_G$	$T (1 - C\Phi/aV)/(1 - C_\Phi\Phi/aV)$	
$(dH/d\Phi)_P$	$T$	$T$
$(dH/d\Phi)_T$	$CT/C_\Phi$	$18CP/3$
$(dH/d\Phi)_V$	$T (C_V - C)/(C_V - C_\Phi)$	$T (H - B)/(E - B)$
$(dH/d\Phi)_V$	$T + aVT/S_V C_V$	$18T/10 + 3bT/(V - b)$
$(dH/d\Phi)_S$	$T + aVT/S (C_S - C_\Phi)$	

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Coefficient	General Expression	Value for Dry Steam
$(dH/dT)_E$	$S(1 - C/C_E)$	$8bS/13c$
$(dH/dT)_G$	$S(1 - C/C_G)$	$S - 13c\Phi/3V\Phi + b\Phi/V$
$(dH/dT)_P$	$S$	$S_0 + 130acP/9T$
$(dH/dT)_*$	$S(1 - C/C_*) = aV/\ell$	$13aV/3T$
$(dH/dT)_V$	$S(1 - C/C_V)$	$S(1 - CP/S_0T)$
$(dH/dT)_S$	$S(1 - Cdp/dt)$	$S - SQ(1b - st)/aV^2T$
$(dH/dV)_E$	$aT(C_E - C)/C_*(C_E - C_V)$	$- aE/(V - b)$
$(dH/dV)_G$	$aT(C_G - C)/C_*(C_G - C_V)$	
$(dH/dV)_P$	$aT/C_*$	$13aP/3$
$(dH/dV)_*$	$- a^2VT/S_V C_V C_*$	$- 13aPV/10(V - b)$
$(dH/dV)_T$	$aTC/C_*C_V$	$aP(SCP/10T)$
$(dH/dV)_S$	$aT(C_S - C)/C_*(C_S - C_V)$	
$(dP/dX)_Z$	$1/(dX/dP)_Z$	See Reciprocals
$(dQ/dE)_Z$	$T/(dE/d\Phi)_Z$	
$(dQ/dG)_Z$	$T/(dG/d\Phi)_Z$	
$(dQ/dH)_Z$	$T/(dH/d\Phi)_Z$	
$(dQ/dP)_Z$	$T(d\Phi/dP)_Z$	See $(d\Phi/dP)_Z$
$(dQ/d\Phi)_Z$	$T$	$T$
$(dQ/dT)_E$	$S_E = S(1 - C_*/C_E)$	$3S(V - b)/13c$
$(dQ/dT)_G$	$S_G = S(1 - C_*/C_G)$	$S(1 - 3T\Phi/13aPV)$
$(dQ/dT)_H$	$S_H = S(1 - C_*/C) = -qV/C$	$- aV/C$
$(dQ/dT)_P$	$S_P = S_V C_V/(C_V - C_*)$	$13R/3 + 130acP/9T$
$(dQ/dT)_V$	$S_V = S(1 - C_*/C_V)$	$(E - B)S/S_0T$
$(dQ/dT)_S$	$S_S = S(1 - C_*/C_S)$	$S(1 - 3(H - st)/13aPV)$
$(dQ/dV)_Z$	$T(d\Phi/dV)_Z$	See $(d\Phi/dV)_Z$
$(d\Phi/dE)_Z$	$1/(dE/d\Phi)_Z$	See Reciprocals
$(d\Phi/dG)_Z$	$1/(dG/d\Phi)_Z$	" "
$(d\Phi/dH)_Z$	$1/(dH/d\Phi)_Z$	" "
$(d\Phi/dP)_E$	$(S/T)(C_E - C_*)$	$- q(V - b)/T$
$(d\Phi/dP)_G$	$(S/T)(C_G - C_*)$	$aVS/T\Phi - 3S/13P$
$(d\Phi/dP)_H$	$- aV/T$	$- aV/T$
$(d\Phi/dP)_T$	$- SC_*/T = - a(dV/dT)_P$	$- 3S/13P$
$(d\Phi/dP)_V$	$S_V C_V/T = - a(dV/dT)_*$	$10a(V - b)/8T$
$(d\Phi/dP)_S$	$(S/T)(C_S - C_*)$	$aVS/(H - st) - 3S/13P$
$(d\Phi/dQ)_Z$	$1/T$	$1/T$
$(d\Phi/dT)_Z$	$(1/T)(dQ/dT)_Z$	See Specific Heats
$(d\Phi/dV)_E$	$a(C_E - C_*)/C_*(C_E - C_V)$	$aP/T$
$(d\Phi/dV)_G$	$a(C_G - C_*)/C_*(C_G - C_V)$	

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Coefficient	General Expression	Value for Dry Steam
$(d\Phi/dV)_H$	$a(C - C_*)/C_*(C - C_V)$	$aP/T(1 - 10b/13V)$
$(d\Phi/dV)_P$	$a/C_* = a(dP/dT)_*$	$13aP/3T$
$(d\Phi/dV)_T$	$a/C_V = a(dP/dT)_V$	$3aP/6_0T$
$(d\Phi/dV)_S$	$a(C_S - C_*)/C_*(C_S - C_V)$	
$(dT/dE)_Z$	$1/(dE/dT)_Z$	See Reciprocals
$(dT/dG)_Z$	$1/(dG/dT)_Z$	" "
$(dT/dH)_Z$	$1/(dH/dT)_Z$	" "
$(dT/dP)_Z$	See Cooling-Effects on first page	
$(dT/d\Phi)_Z$	$T/(dQ/dT)_Z$	See Specific Heats
$(dT/dV)_Z$	$1/(dV/dT)_Z$	See Reciprocals
$(dV/dE)_Z$	$1/(dE/dV)_Z$	" "
$(dV/dG)_Z$	$1/(dG/dV)_Z$	" "
$(dV/dH)_Z$	$1/(dH/dV)_Z$	" "
$(dV/dP)_E$	$-(SC_*/aT)(C_V - C_E)$	$-(V - b)/P$
$(dV/dP)_G$	$-(SC_*/aT)(C_V - C_G)$	$-(V/P)(RT/aPV - 3S/13\Phi)$
$(dV/dP)_H$	$-(SC_*/aT)(C_V - C)$	$-(V - 10b/13)/P$
$(dV/dP)_*$	$-(SC_*/aT)(C_V - C_*)$	$-10(V - b)/13P$
$(dV/dP)_T$	$-(SC_*/aT)C_V$	$-(V + c - b)/P$
$(dV/dP)_T$	$-C_V V/T - C_V SC_*/aT$	$-RT/aP^2$
$(dV/dP)_S$	$-(SC_*/aT)(C_V - C_S)$	
$(dV/d\Phi)_Z$	$1/(d\Phi/dV)_Z$	See Reciprocals
$(dV/dT)_E$	$(SC_*/aT)(1 - C_V/C_E)$	$-3S(V - b)/13acP$
$(dV/dT)_G$	$(SC_*/aT)(1 - C_V/C_G)$	$(3S/13aP)(1 - S_0T\Phi/aPVS)$
$(dV/dT)_H$	$(SC_*/aT)(1 - C_V/C)$	$-(V - 10b/13)/CP$
$(dV/dT)_P$	$SC_*/aT$	$3S/13aP$
$(dV/dT)_T$	$V/T + SC_*/aT$	$R/aP + 10c/3T$
$(dV/dT)_*$	$-S_V C_V/aT$	$-10(V - b)/3T$
$(dV/dT)_S$	$(SC_*/aT)(1 - C_V/C_S)$	

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